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A versatile synthetic approach towards the synthesis of new polycyclic aromatic hydrocarbons using Scholl, Grignard and Umpolung chemistries

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A Versatile Synthetic Approach Towards the Synthesis of New Polycyclic Aromatic Hydrocarbons Using Scholl, Grignard and Umpolung Chemistries

BY

Joseph M. Dunn

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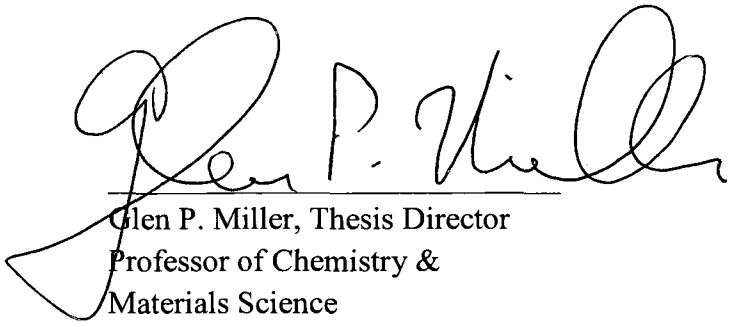

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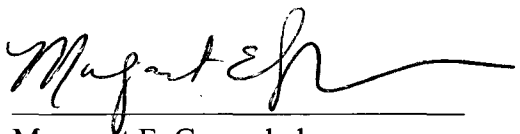

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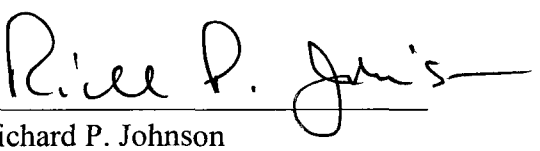

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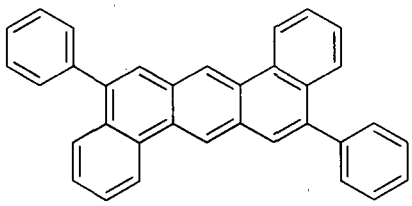

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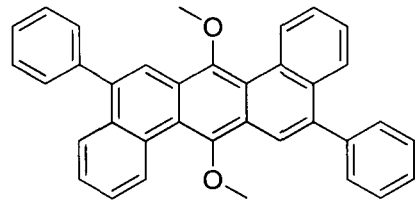

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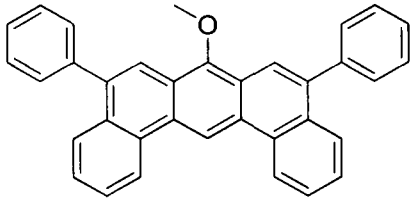

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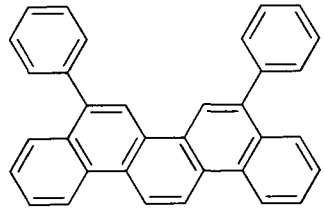

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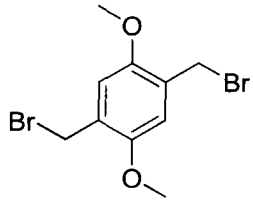

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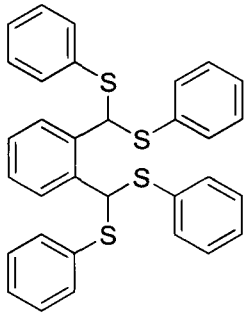

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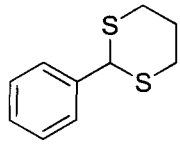

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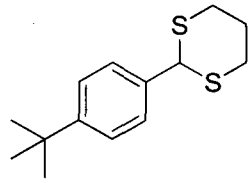

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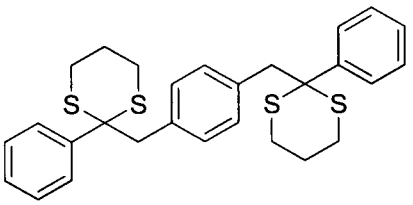

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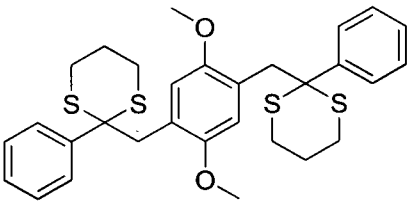

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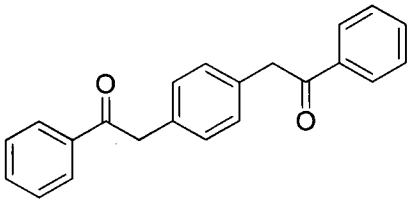

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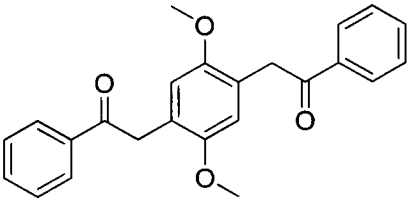

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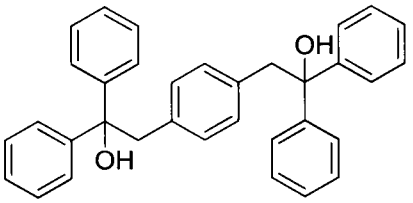

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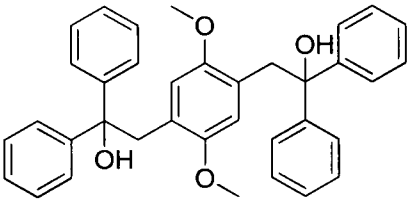

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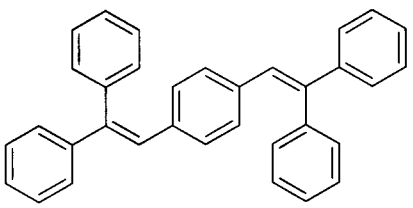

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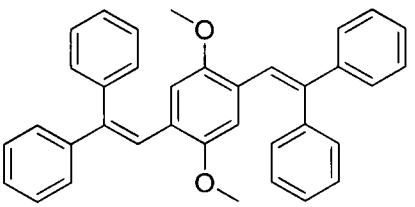

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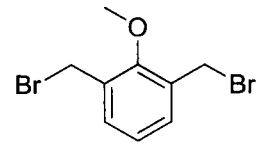

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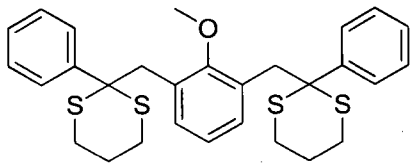

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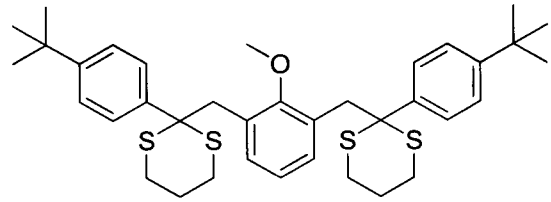

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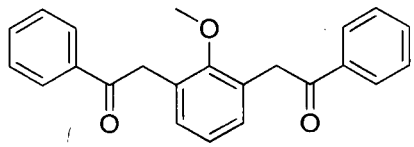

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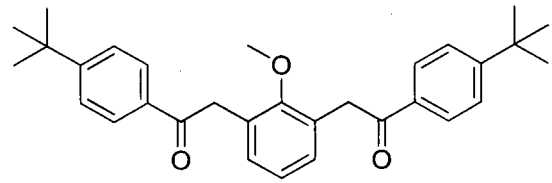

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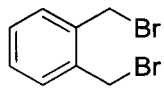

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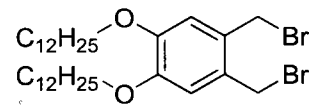

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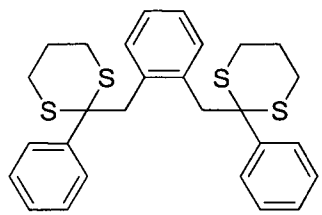

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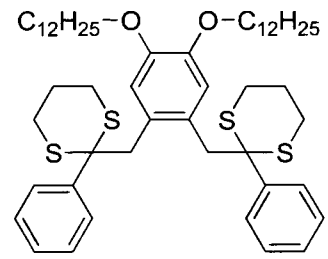

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ABSTRACT

A Versatile Synthetic Approach Towards the Synthesis of New Polycyclic Aromatic Hydrocarbons Using Scholl, Grignard and Umpolung Chemistries

By

Joseph M. Dunn

University of New Hampshire, September, 2010

The Synthesis of Dibenzo anthracenes 3, 7-diphenyldibenzo[a,h] anthracene (**1**) and 3,6-diphenyl-9-methoxydibenzo [a,j] anthracene (**2**) as well as a phenyl substituted picene (**3**) was attempted utilizing an original, generic, scheme. An Umpolung reaction between a 1,3-dithiane and a variety of dibromomethyl benzene hubs was performed to generate the carbon framework of **1, 2** and **3**. Deprotection of the thioacetal groups yielded a carbonyl product which upon Grignard addition and dehydration could potentially be converted to the desired product. The proposed synthetic design allows for a variety of substitution patterns about the parent PAHs, without adding synthetic steps.

CHAPTER 1. INTRODUCTION

1.1 ACENE CHEMISTRY

1.1.1 LITERATURE SURVEY

Acenes and acene derivatives have been the subject of much interest over the last century. Acenes can be described as linearly fused polycyclic aromatic hydrocarbons, originally described by Clar as having the fewest localized resonant sextets per number of aromatic rings.[1] In principle, acenes can vary in size from anthracene, with three fused aromatic rings, to an infinite number of linked aromatic rings (**Figure 1**). Isolated from crude petroleum, anthracene, is the only naturally occurring acene. Larger acenes such as tetracene and pentacene, with four and five aromatic rings respectively, can be synthesized. They are however, unstable in the presence of oxygen and light as they rapidly photooxidize and/or photodimerize.[2, 3]

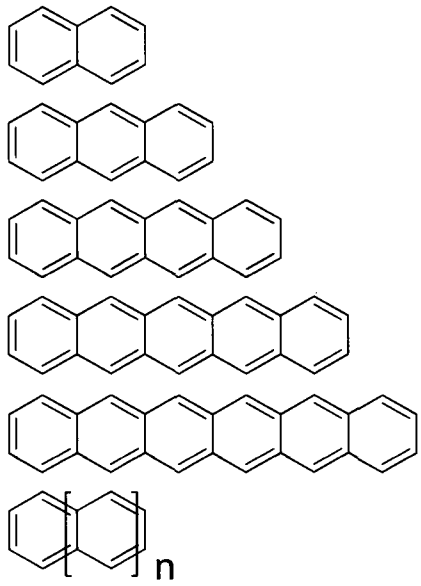
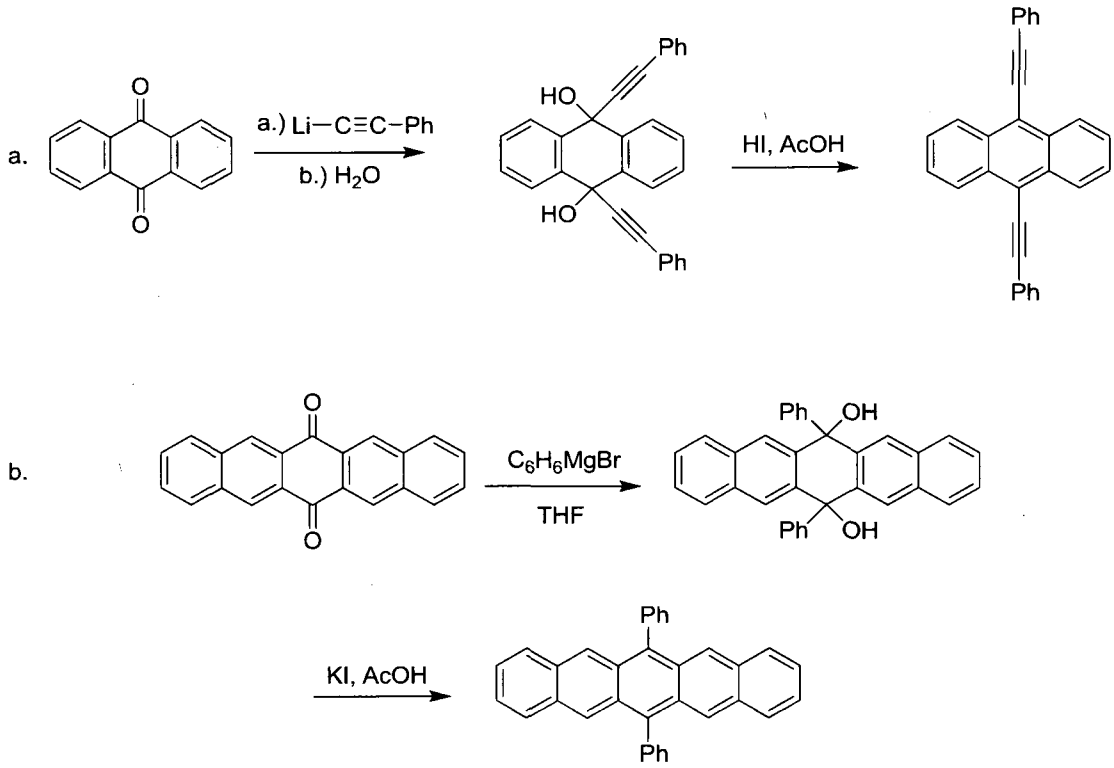


Figure 1: Acene series through hexacene shown.

Acenes have been shown to exhibit semiconducting properties with high charge-carrier mobilities.[4-6] Due to their semiconducting properties, both tetracene and pentacene have been utilized in organic field effect transistor (OFET), organic light emitting diode (OLED) and organic photovoltaic (OPV) applications.[7-10] However, degradation of pentacene and tetracene in the presence of light and air has been a major limitation in device production.[11] Thus, development of photooxidatively resistant acenes is a high priority in materials science. The fact that unsubstituted acenes suffer from poor solubility in common solvents has also led to a great deal of synthetic chemistry devoted to improving solubility, while reducing reactivity and increasing resistance to degradation.[12-17] It has been shown that functionalizing the center ring of odd-numbered acenes is imperative. The center rings in acenes are known theoretically and experimentally to be the most reactive. [18, 19] Common reactions include Diels-Alder type cycloaditions. Photooxidations likely involve Diels-Alder cycloadditions of $^1O_2$.[17]

The classical method to functionalize the central ring of an acene starts with the appropriate quinone precursor. This chemistry was first developed *circa* 1940 and has continued since.[14, 20-23] One example is the addition of lithium phenylacetylide to 9,10-anthraquinone which results in a diol species that can be reduced to a 9,10-disubstituted anthracene product (**Scheme 1a**).[20] Another approach to functionalize acene quinones is *via* Grignard addition as first reported by Allen and Bell[12] (**Scheme 1b**).



Scheme 1: a.) Synthesis of 9,10-bis(phenylethynyl)anthracene from 9,10-anthraquinone, b.) Synthesis of 6,13-diphenylpentacene from 6,13-pentacenequinine.

Perhaps most notable of the recently prepared semiconducting acenes is 6,13-ditriisopropylsilylethynylpentacene (TIPS pentacene) synthesized by Anthony and coworkers in 2001 (**Figure 2**).[24] Until recently, TIPS pentacene was the most common acene employed in OFET devices.

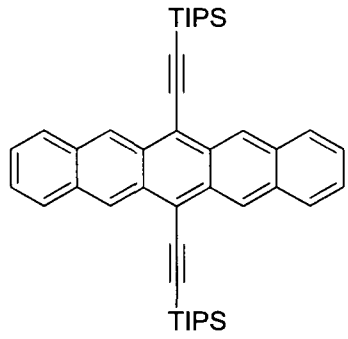


Figure 2: TIPS pentacene synthesized by Anthony.

The semiconducting nature of an acene is dependent on its band gap. The band gap is the energy difference between valence and conduction bands in a solid.[25] It is closely related to HOMO-LUMO gaps in individual molecules. As acenes become larger, their band gaps decrease due to extended conjugation, making them more suitable semiconductors. Larger acenes are therefore considered to be important synthetic targets.[26] Substituents that solublize and protect acenes from degradation can also impact an acene's band gap.[17]

Until recently, access to acenes larger than pentacene has been limited as their syntheses are challenging, and more importantly, they are susceptible to rapid photooxidative degradation. The first reported isolation of hexacene and heptacene, was by Neckers and co-workers who prepared unsubstituted hexacene and heptacene in a polymethylmethacrylate (PMMA) matrix.[27] Using this technique, hexacene and heptacene were shown to have lifetimes of four and twelve hours, respectively. Anthony and co-workers prepared silyethynyl substituted hexacene and heptacene derivatives that were sufficiently stable as solids that they could be studied by x-ray crystallography.[28, 29] Wudl and co-workers made moderate improvements to Anthony's approach by adding additional phenyl substituents to the heptacene skeleton.[30] Miller and co-workers

prepared the longest live heptacene derivative by utilizing aryl thio substituents in conjunction with ortho dialkylphenyl substituents.[31] Organothio substituents are considerably more effective than silylethynyl substituents and ortho dialkylphenyl substituents are better than simple phenyl substituents at protecting acenes from photooxidation. Very recently, Miller and co-workers were able to isolate a photooxidativly resistant nonacene derivative using a combination of arylthio and ortho dimethylphenyl substituents (**Figure 3**).[32]

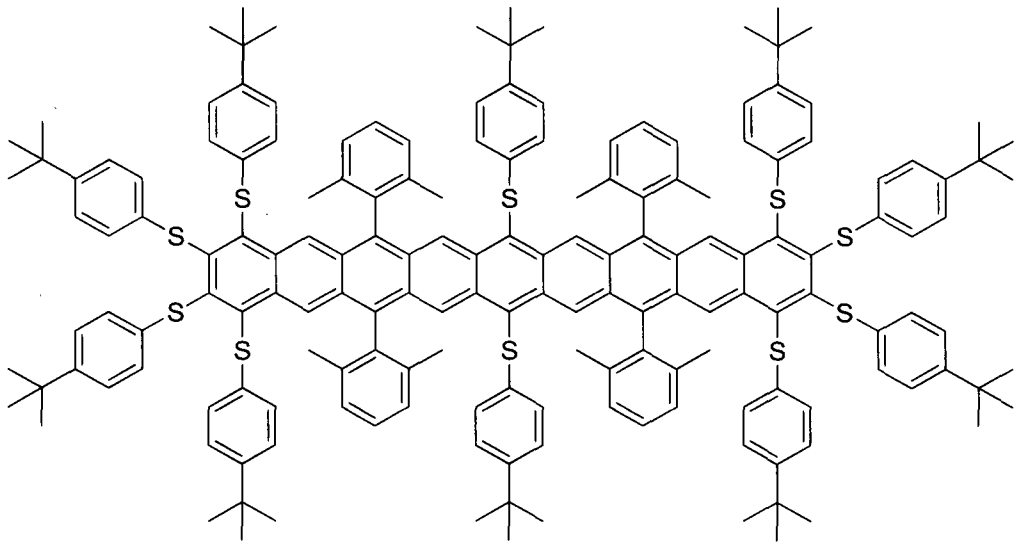


Figure 3: Photooxidatively resistant nonacene synthesiszed by Miller, Kaur and co-workers.

1.1.2. ANGULAR BENZENES

In order to synthesize new acenes with greater solubility and photooxidative resistance, new synthetic strategies must be developed. In conjunction with conventional functionalization of acenes, the fusion of angular benzenes to an acene core has proven beneficial in the search for more photooxidatively resistant acenes.[33] In 1980 Biermann

and Schmidt reported the rates of Diels-Alder reactions involving a variety of PAHs and maleic anhydride. The Diels-Alder reactivity of PAHs has been shown to correlate with the ease of photooxidative decay.[34] Biermann and Schmidt showed that fusing benzene rings in an angular fashion to the ends of an acene decreases its Diels-Alder reactivity. Likewise, the addition of angular benzenes to acenes should also lead to enhanced photooxidative resistance. Two angular benzenes can be added to anthracene in several unique ways. It was shown that placing them on opposite ends to produce dibenzo[a,h]anthracene and dibenzo[a,j]anthracene had a greater impact than when they were fused to the same side to produce dibenzo[a,c]anthracene. The spatial location of the angular benzenes (ie., *syn* or *anti*) had no effect on the reactivities of the species **(Figure 4)**.

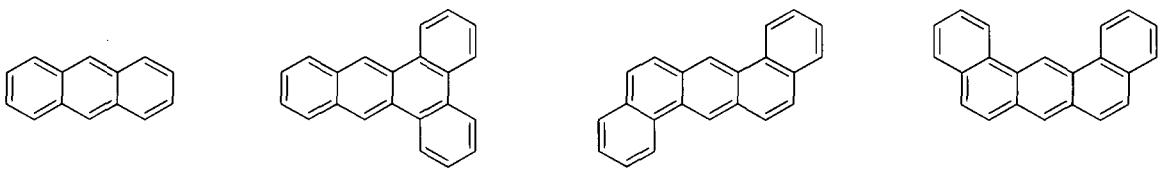


Figure 4: Rates of Diels-Alder reactivity for anthracene derivatives bearing fused angular benzenes. Second order rate constants are factored by 10^6 for simplicity.

Bierman and Schmidt concluded that Clar's sextet concept provides insight into the decrease in reactivity.[1] Clar suggested that as an acene is linearly annelated there is a gradual loss of benzenoid character. Clar identifies benzenoid character as 6 π electrons in a ring and represents it with a circle. In a linear acene, only one circle can be included and the electronic delocalization is symbolized with an arrow **(Figure 5)**. As with each

new angular annelation of a benzene ring, a new sextet is generated, thus creating increased benzenoid character and decreased reactivity.

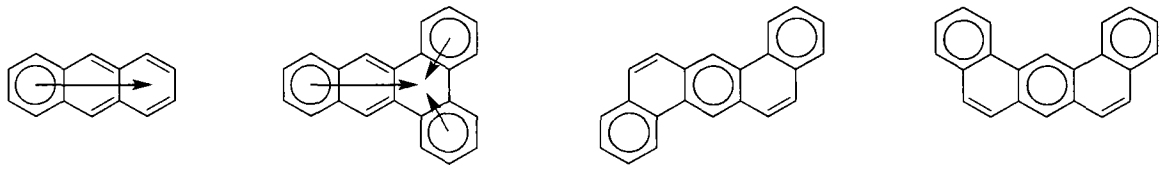


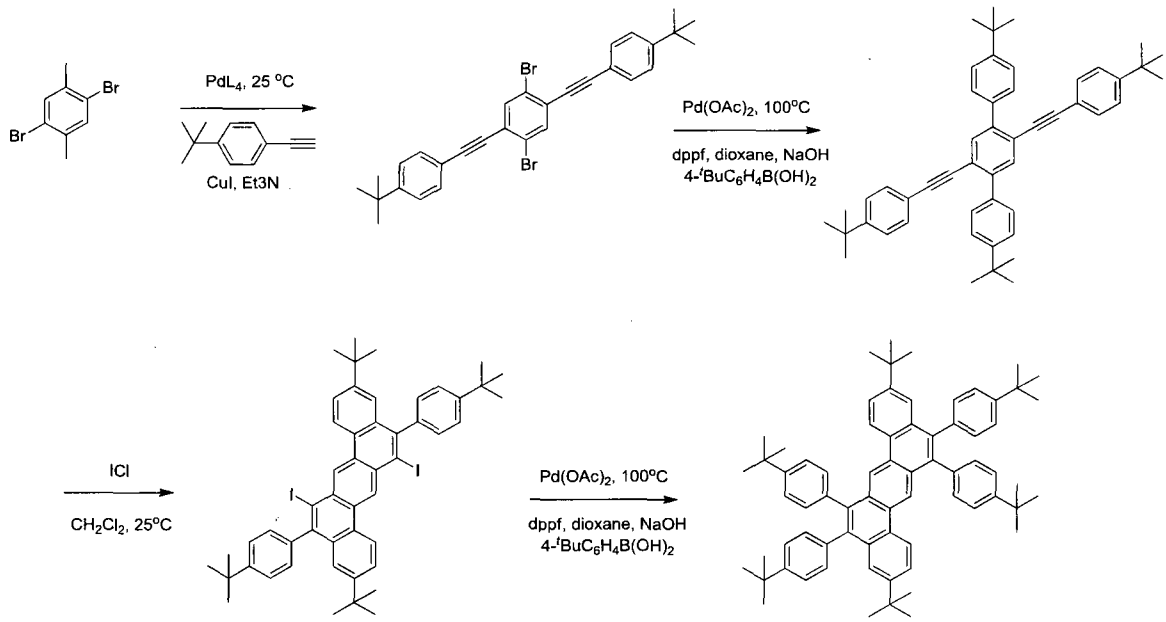
Figure 5: Anthracene derivatives with various fused angular benzene rings. Clar's aromatic sextets are represented.

It is important to keep in mind that although there is a decrease in reactivity and likely an increase in photooxidative resistance, the anthracene moiety is still present and the molecule still retains a HOMO-LUMO gap that make it potentially useful. For this reason the addition of angular benzene is seen as an effective modification of an acene moiety, resulting in improved photooxidative resistance while not significantly impacting the band gap or other electronic properties.

Angular benzo acenes such as dibenzo[a,h]anthracene and dibenzo[a,j]anthracene were reported as early as 1958 by LaBudde and Heidelberger, who were examining the toxicity of PAHs in rabbits.[35] Early syntheses of various PAHs have been reviewed extensively, most notably by Clar in his two-volume book set "Polycyclic Hydrocarbons".[1] As PAH's have gained interest in the scientific community, a great deal of attention has been paid to their synthesis. Early synthetic techniques included flash vapor pyrolysis (FVP),[36] reductive cyclization,[37] annelation,[38] and cycloaddition[39] to name a few. Most early methods involved harsh conditions and suffered from low yields and poor selectivity.[40] More recent synthetic methods include Suzuki and other metal-catalyzed coupling methods[41] as well as ring-closing olefin metathesis,[42] and metal catalyzed cyclization.[43] As reported earlier, the solubility of PAHs decreases as benzo

groups are added, thus additional functionalization of PAHs would be necessary for their utilization in materials. The functionalization of acenes with angular benzenes requires new methods, one of which is detailed here.

Many syntheses of PAH's incorporate functional groups as activators to promote ring formation, as in oxidative photocyclization.[44] Other functional groups such as the *t*-butyl group simply serve to increase solubility. Recently Hseuh, *et. al.* reported an efficient synthesis of a *t*-butylphenyl substituted 1,2,5,6-dibenzoanthracene (**Scheme 2**).[45] Hseu *et. al.* utilized Sonogashira coupling[46], followed by Suzuki coupling,[47] then ICl-mediated benzannulation,[48, 49] and finally a second Suzuki coupling step.



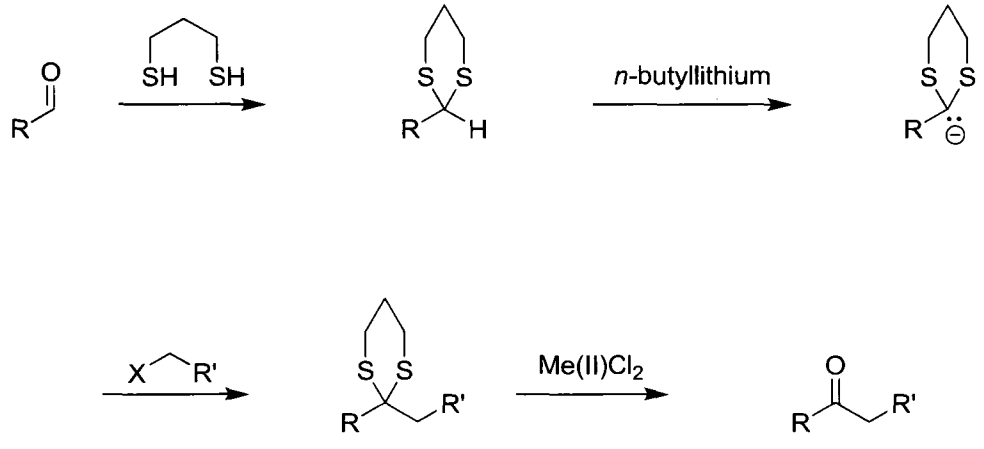
Scheme 2: Synthesis of 3,10-di-*t*-butyl-5,6,12,13-tetrakis(4-tert-butylphenyl)benzo[k]tetraphene from 1,4-dibromo-2,5-dimethylbenzene.

Hseuh was not interested in this specific molecule but took the synthesis further to obtain a functionalized rubicine moiety. Though not his intention, Hseuh designed a novel synthesis for a potentially useful acene. Hseuh's PAH gains photooxidative

resistance due to the angular benzenes, and has greater solubility than its unsubstituted PAH counterpart due to the *t*-butyl phenyl substituents.

1.2. UMPOLUNG CHEMISTRY

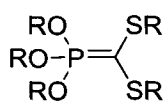
Umpolung chemistry refers to a temporary reversal in polarity of a functional group in order to form C-C bonds that would otherwise be impossible.[50-53] The idea was first presented by Corey and Seebach in 1965.[52] This reversal in polarity generally refers to a modification of an electrophile to form a nucleophile, capable of attacking another electrophile (**Scheme 3**). Umpolung approaches have been applied extensively in the synthesis of complex natural products, due to their versatility and uniqueness.[54] The term umpolung only refers to a concept, thus there are several variations and functionalities that apply the umpolung principle.



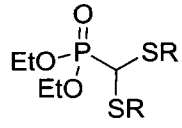
Scheme 3: Example of umpolung reaction, a formyl aldehyde is made nucleophillic allowing it to undergo S_N2 chemisty with a 1^o halide.

The formylation of aldehydes via phosphorus substitution has been shown to be an effective tool in synthesis and is fundamentally based on the umpolung principal.

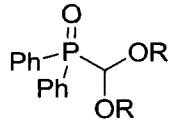
There are several phosphorus stabilized synthons which serve as anion equivalents, the first of which, phosphate ylides, were reported by Lemal and Banitt in 1964.[55] These ylids were used in the homologation of aldehydes in olefin reactions. Phosphonate-stabilized carbanions also served as synthons for the formation of ketene S,S- or O,S-acetals.[56] Metellated phosphane oxides have also been shown to yield ketene O,O-acetals in reactions with aldehydes (**Figure 6**).[57]



Phosphite ylid



Phosphonate-stabilized carbanion

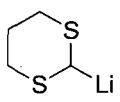


Metellated phosphane oxides

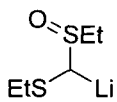
Figure 6: Phosphorus substituted anions, used in Umpolung chemistry.

Both phosphonate-stabilized carbanions and metellated phosphane oxides can be deprotonated with a strong base, usually an alkyl lithium, to yield a carbanion capable of reacting with an electrophile.[54]

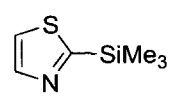
Formyl anion equivalents are the most common example of the umpolung principal and there are many variations. The most common anion equivalent would be 1,3-dithians. Other anion equivalents include lithiated sulfoxides,[58] lithiated or silylated thiazoles,[59] and benzo-triazoles (**Figure 7**).[60-62]



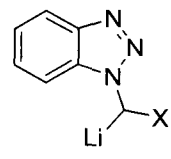
1,3-dithiane



lithiated sulfoxide



silylated thiazole



X= OPh, SMe

benzotriazole

Figure 7: Common formyl anion equivalents

Furthering their usefulness, anion equivalents can also be chiral as in N-Boc-thiazolidine [in the presence of (-)-spartene],[63] chiral metellated thiazolidine, or lithiated thiomethyloxazolidinone (**Figure 8**).[64] When anion equivalents are made chiral, they can be utilized in enatioselective natural product synthesis. Lithiated dithioacetals are the most common anion equivalent, with 1,3-dithioacetal being the most widely used.

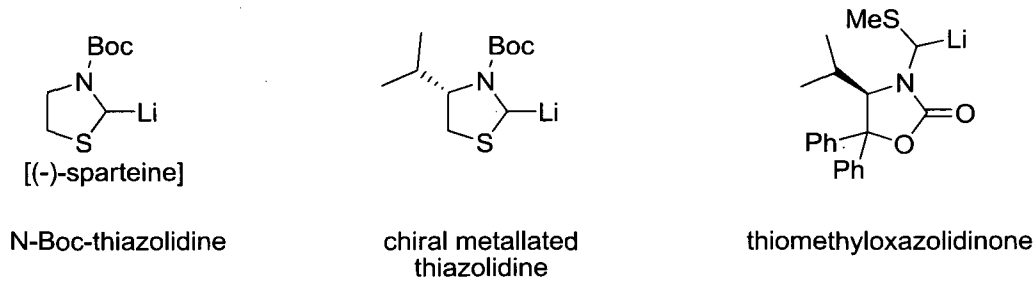


Figure 8: Formyl chiral anion equivalents

Since the introduction of 1,3-dithioacetals as anion equivalents by Corey and Seebach, other thioacetals such as diethylthioacetal and diphenylthioacetal, have been utilized in umpolung reactions (**Figure 9**).[65-67]

Figure 9: Lithiated thioacetal anion equivalents.

Thioacetals are generally formed via protection of an aldehyde or ketone.[68] Thioacetals gain anionic character after deprotonation by a strong base. *n*-Butyl lithium, phenyl lithium and lithium diisopropylamide (LDA) are all commonly used.[54, 69-76] The anions that are generated are strongly stabilized by adjacent sulfur atoms, giving them

properties equivalent to acyl anions.[70] Thioacetals are versatile, stable and generally react in good yields with aldehydes as well as primary halides. To date no, umpolung chemistry has been applied to the synthesis of PAHs.

1.3. SCHOLL REACTION

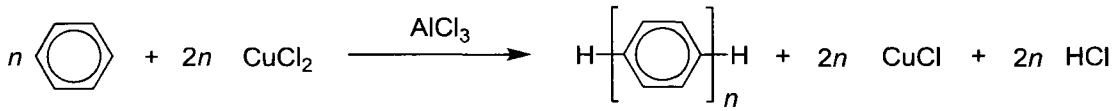
1.3.1. HISTORY

A reaction that has potential application in the synthesis of benzo fused acenes is the Scholl reaction. First reported in 1910 by Scholl and Seer,[77-79] the use of aluminum trichloride melts with atmospheric oxygen as an oxidant led to the fusion of biaryl rings (**Scheme 4**).

Scheme 4: Genaric Scholl reaction

In the 1960s, Kovacic optimized the reaction by employing copper(II) chloride instead of atmospheric oxygen as the oxidant, and aluminum trichloride in the polymerization of benzene (**Scheme 5**).[80-84] Kovacic identified that a strong acid, usually a Lewis acid, and an oxidant are necessary to form a bond between unfunctionalized aryl vertices.[85] Kovacic provided the makeup of mild conditions that can produce a highly selective oxidative cyclodehydrogenation of oligophenylenes to PAHs, known today as the Scholl reaction. Common reagents used in the Scholl reaction include but are not limited to: $FeCl_3$ in CH_2Cl_2, $CuCl_2$ or $Cu(OSO_2CF_3)_2$ with $AlCl_3$ in CS_2, $MoCl_5$ with or without

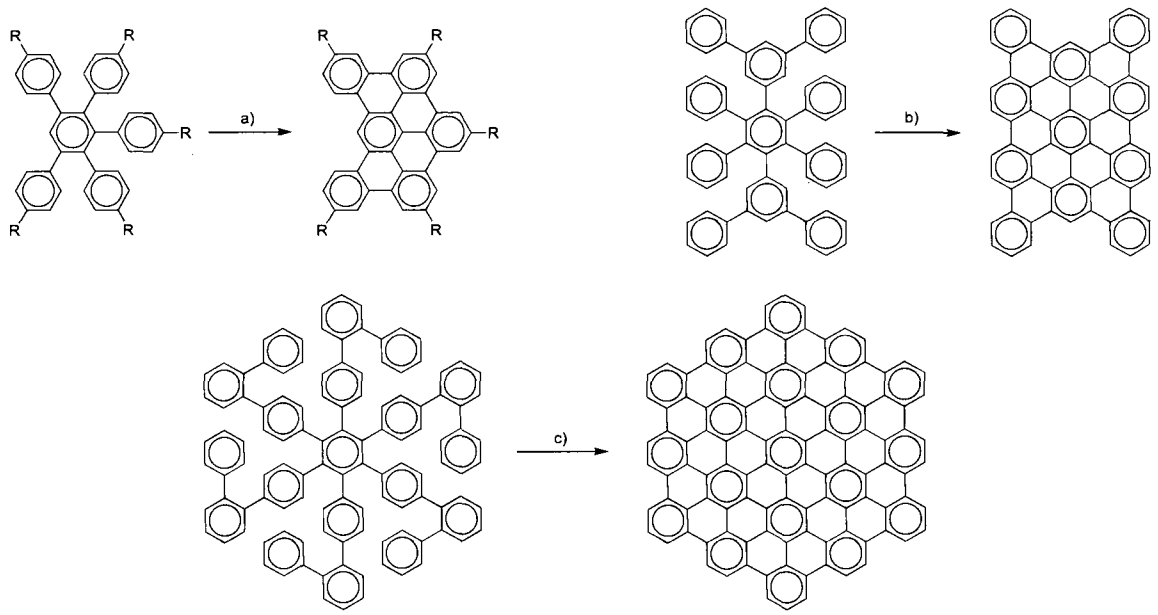
$TiCl_4$ in CH_2Cl_2, $(CF_3COO)_2I^{III}C_6H_5$ (PIFA) with $BF_3 \cdot Et_2O$ in CH_2Cl_2, $Pb(OAc)_4/BF_3 \cdot Et_2O$ MeCN, $Tl(O_2CCF_3)_3$ in CF_3CO_2H, $Tl(O_2CCF_3)_3/BF_3 \cdot Et_2O$ in organic solvents,[86] as well as DDQ with $MeSO_3H$ in CH_2Cl_2.[87] Today, Scholl reactions are utilized almost exclusively in an intramolecular fashion, as intermolecular reactions are non-selective and generally yield oligomers.[84, 88]



Scheme 5: Oxidative polymerization of benzene under Kovacic conditions.

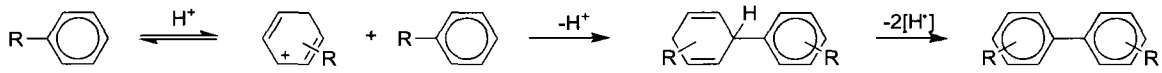
1.3.2. APPLICATIONS

The Scholl reaction has gained notoriety in the chemical literature as an efficient method for expanding the π-electron conjugation of an already large aromatic system. Müllen, a pioneer in the field of large PAH compounds, has prepared many large PAHs utilizing Scholl chemistry.[89] Intramolecular Scholl reactions require that the desired carbon framework is in place as the number of carbons does not change in the reaction. Müllen has shown that oligophenylene derivatives can undergo complete intramolecular cyclodehydrogenation to form all-benzenoid aromatic products in a single step (**Scheme 6**).[90, 91] Presently a record of 126 new C-C bond have been formed in a single step by Müllen using the Scholl reaction.[92]



Scheme 6: Examples of Scholl reactions. (a) $FeCl_3$, CH_2Cl_2, 25 °C, 30 min; (b) $Cu(OSO_2CF_3)_2$, $AlCl_3$, CS_2, 25 °C, 24 h; (c) $Cu(OSO_2CF_3)_2$, $AlCl_3$, CS_2, 25 °C, 24 h.

Insight into the mechanism for the Scholl reaction has been provided by King and co-workers who have studied this reaction extensively.[86, 93-95] King proposes an arenium cation mechanism which calls for the protonation of an oligophenylene, resulting in an electrophilic σ complex which reacts with another aromatic core to generate a new C-C bond. Deprotonation followed by dehydrogenation restores aromaticity to give the desired product (**Scheme 7**).[94] King also surmised that in cases such as Müllen's where



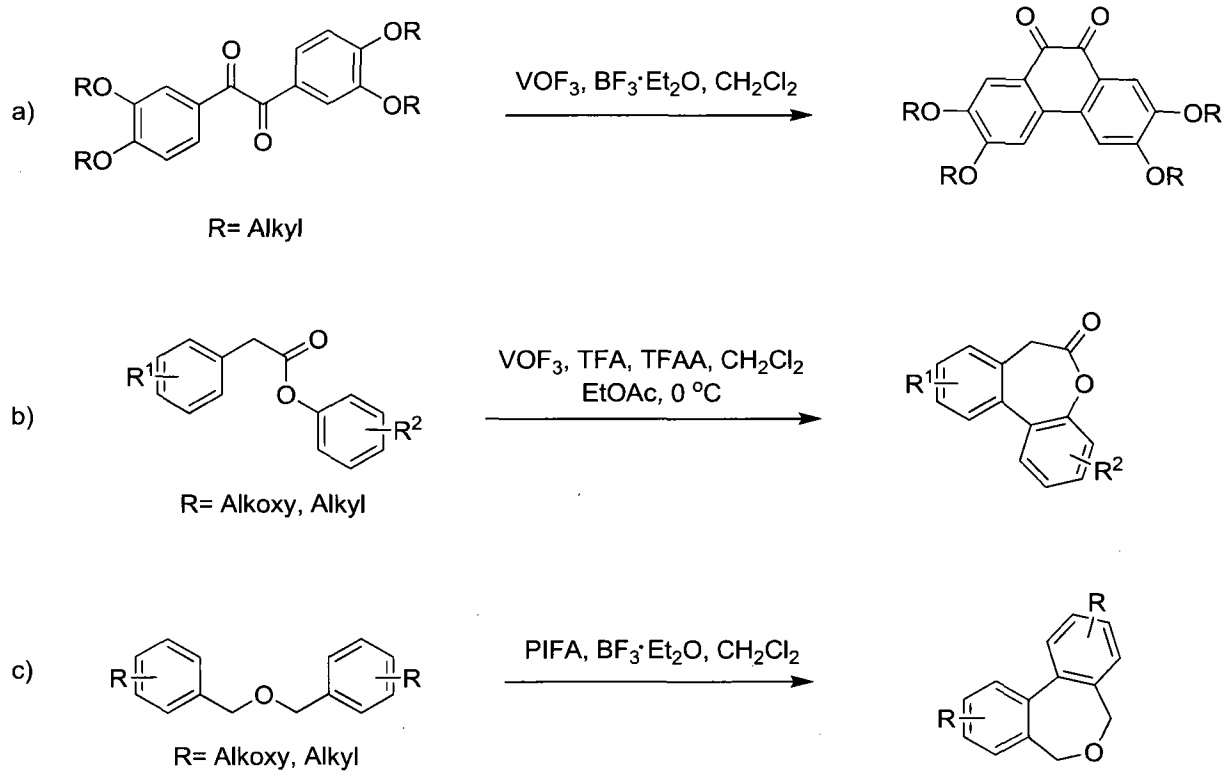
Scheme 7: Proposed arenium cation mechanism of a Scholl reaction.

multiple C-C bonds are formed in an aromatic framework, bond formation is not concerted but successive. The ground state energy of the product formed by each new C-

C bond is exponentially lower after each cyclization. This is related to an increase in resonance energy per π electron.[96]

1.3.3. NON AROMATIC SCHOLL REACTIONS

Though Scholl reactions have been predominantly used in large substituted, or unsubstituted PAH syntheses,[87, 97-101] there are many reports in the literature of non-aromatic products resulting from a Scholl reaction.[102-105] In a synthesis where the Scholl reaction has been employed and the product does not gain aromaticity, exotic reactants are necessary. Vanadium(V) oxytrifluoride has been utilized in such cases. Various diphenyl diketone derivatives have undergone oxidative cyclization to the corresponding phenanthrene-9,10-diones, using VOF_3 or PIFA, $BF_3 \cdot Et_2O$, in CH_2Cl_2 (**Scheme 8a**) as reported by Foster *et. al* and



Scheme 8: a). diphenyl diketone oxidative cyclization to phenanthrene-9,10-dione. b). ester tethered di-aryl coupling reaction. c). coupling of 1,3-diarylpropanes to a dibenzoheterocycle.

Lavigueur *et. al.*[102, 104] An even more exceptional variation on the Scholl reaction comes from Taylor *et. al.* who were able to couple ester tethered diaryl species as shown in **Scheme 8b**,[103] as well as the coupling of 1,3-diarylpropanes to their corresponding dibenzoheterocycles (**Scheme 8c**).[105] Though the later two examples contain hetero-atoms in the newly formed ring, it is important to note that it is not necessary to gain aromaticity, for the reaction to proceed.

In the synthesis of novel acene derivatives, it will be necessary to employ variations on existing chemistries. Umpolung methodologies, combined with the Scholl reaction will be used here in the pursuit of a variety of novel acenes derivatives.

CHAPTER 2. Results and Discussion

We have attempted to utilize Umpolung methodologies to design a novel, concise, synthetic scheme that could lead to a variety of PAHs. We employed thioacetal anion equivalents which are capable of forming carbon-carbon linkages that would otherwise be impossible. Our strategy is to extend aromatic character from a central aryl building block or "hub" (**Figure 10**). We identified a single benzene ring with two equivalent substituents to be the simplest hub to develop our methodology. In an attempt to design a generic scheme capable of yielding a variety of products, the implementation of a hub is crucial. Simply by varying the position of the substituents about benzene a new carbon framework will form while the synthetic steps remain the same. Our scheme is capable of synthesizing unique PAHs in as few as five steps from inexpensive reagents starting with eight carbons or fewer (**Scheme 9**).

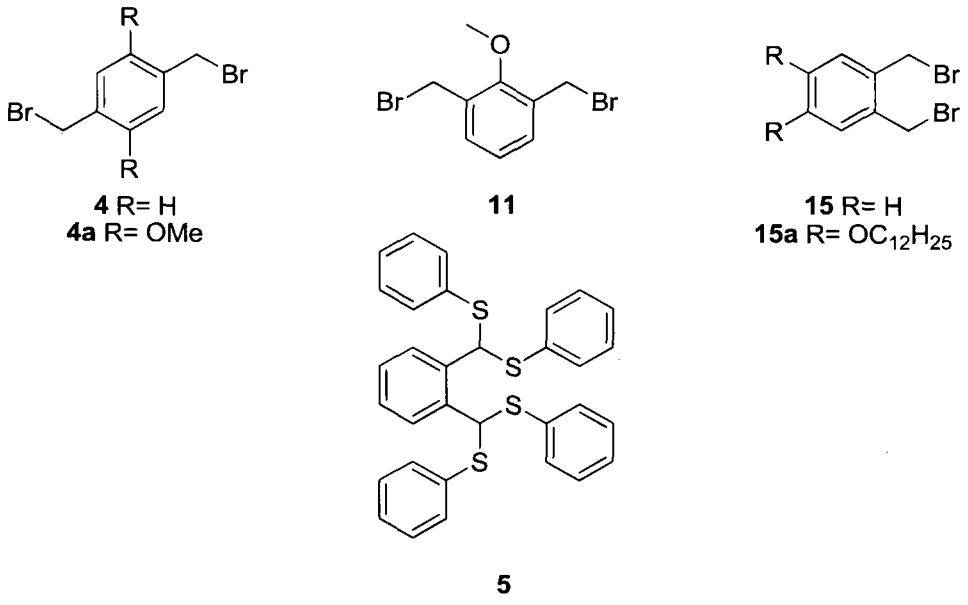
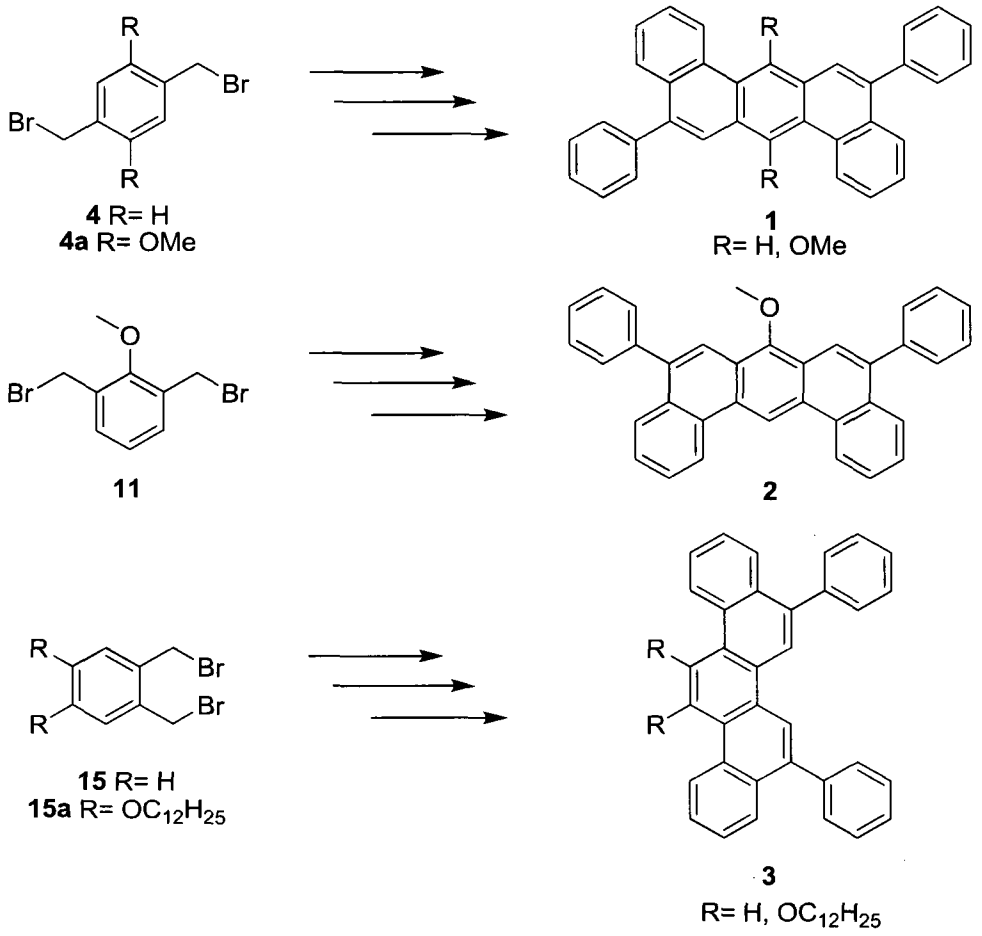


Figure 10: Hub geometries to be studied.

The thioacetal product formed from the umpolung reaction would have the desired carbon backbone to access a PAH architecture. The Scholl reaction will be employed to cyclize the carbon backbone to form the desired PAH. Simply by varying the hub, various PAH structures could be formed from a versatile synthetic sequence (**Scheme 9**). Dibenzo anthracenes 3,7-diphenyldibenzo[a,h]anthracene (**1**) and 3,6-diphenyl-9-methoxydibenzo[a,j]anthracene (**2**) would result from *para* and *meta*-benzene hub substitution, respectively. A phenyl substituted picene (**3**) would result from an *ortho*-benzene hub. Picene maps directly onto armchair carbon nanotubes. Picene thin-films were recently shown to possess interesting electronic properties.[106] They formed field effect transistors that actually performed better upon exposure to air.



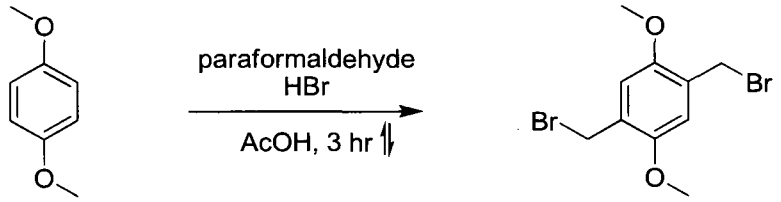
Scheme 9: Targeted molecules from Umpolung synthetic strategy.

2.1. Synthesis of 3,7-diphenyldibenzo[a,h]anthracene (1)

2.1.2. Hub Synthesis

For the synthesis of 3,7-diphenyldibenzo[a,h]anthracene (**1**), α,α′-dibromo-*p*-xylene (**3**) was one of two starting compounds of interest. While **4** is commercially available, the second starting material of interest, α,α′-dibromo-2,5-dimethoxy-*p*-xylene (**4a**), had to be synthesized. The addition of two electron donating methoxy substituents was hoped to facilitate the Scholl reaction at the end of the synthetic sequence. Synthesis of **4a** was achieved through bromomethylation of *p*-methoxybenzene with formaldehyde and hydrobromic acid in acetic acid (**Scheme 10**). After 3 hours of reflux a white

precipitate formed which was cooled to 5 °C and left overnight. Filtration of the white precipitate afforded **4a** in 60% yield with no need for further purification.



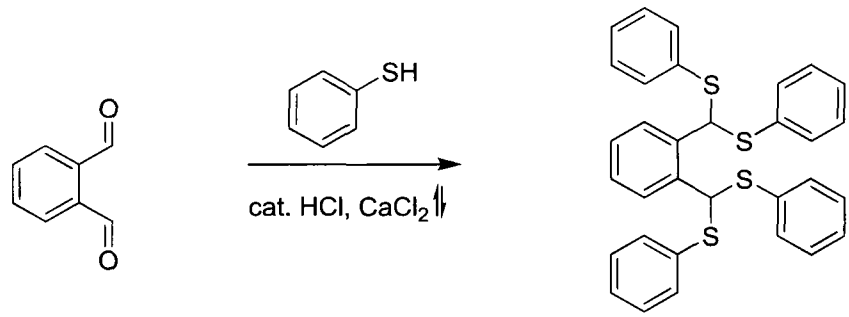
60%
4a

Scheme 10: Synthesis of α,α′-dibromo-2,5-dimethoxy-*p*-xylene (**4a**) from *p*-methoxybenzene.

2.1.2. Umpolung Chemistry

2.1.2.1. Synthesis of Thioacetals

Two literature methods were utilized to generate thioacetals from aldehydes. The first, demonstrated by Zaidi and co workers, involves the condensation of the carbonyl in neat thiophenol.[67] Catalytic hydrochloric acid with anhydrous calcium chloride, was used to convert phthalaldehyde to 1,2-bis(bis(phenylthio)methyl)benzene (**5**) in 81% yield (**Scheme 11**). It should be noted that low molecular weight thiophenols have strong, unpleasant odors and proper ventilation is a necessity. Reactions run in neat thiophenol require a tedious work-up. Aqueous sodium hypochlorite was utilized to neutralize the excess thiophenol.

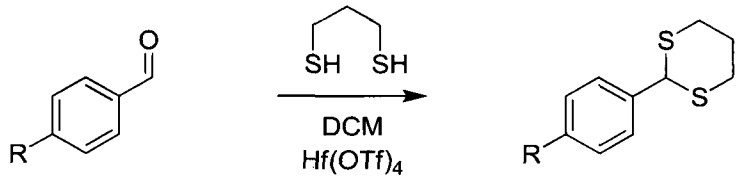


Scheme 11: Synthesis of 1,4-bis(bis(phenylthio)methyl)benzene **5** from excess thiophenol with anhydrous $CaCl_2$ and catalytic HCl.

An alternative method for the generation of thioacetals from aldehydes comes from Wu and Zhu who utilized catalytic hafnium trifluoromethanesulfonate [$Hf(OTf)_4$] with stoichiometric equivalants of the thiol species to generate thioacetals.[65] Because $Hf(OTf)_4$ is highly oxophilic,[107] and has low thiophilicity,[108] it can be used at 0.1 mol % and reactions can be run at room temperature in as little as five minutes. This reaction is run in dichloromethane (DCM), and the thiol species is added in stoichiometric amounts. Consumption of the thiol can be monitored by thin layer chromatography (TLC). With full consumption of the thiol, there is no need to neutralize excess thiol. Thus, this method is preferred over the Zaidis method.

Wu and Zhu's $Hf(OTf)_4$ catalyst was utilized in an attempt to form **5** but only one of the carbonyls was converted to a thiacetal. This was likely due to a steric issue as the bulky nature of the thiophenyl groups presumably hinders the reactivity of the second carbonyl. Conversely, the generation of 2-phenyl-1,3-dithiane (**6**) from $Hf(OTf)_4$ proved to be effective, and could be scaled to gram quantities. Upon scale up, the reaction was allowed to stir overnight to ensure complete conversion to the thioacetal. Workup of the

reaction by filtering through packed celite to remove $Hf(OTf)_4$,yielded **6** and 2-*p*-*t*-butylphenyl-1,3-dithiane (**6a**) as fluffy white powders in 67% and 71%, yield respectively (**Scheme 12**).



6 R= H 67%
6a R= *t*-butyl 71%

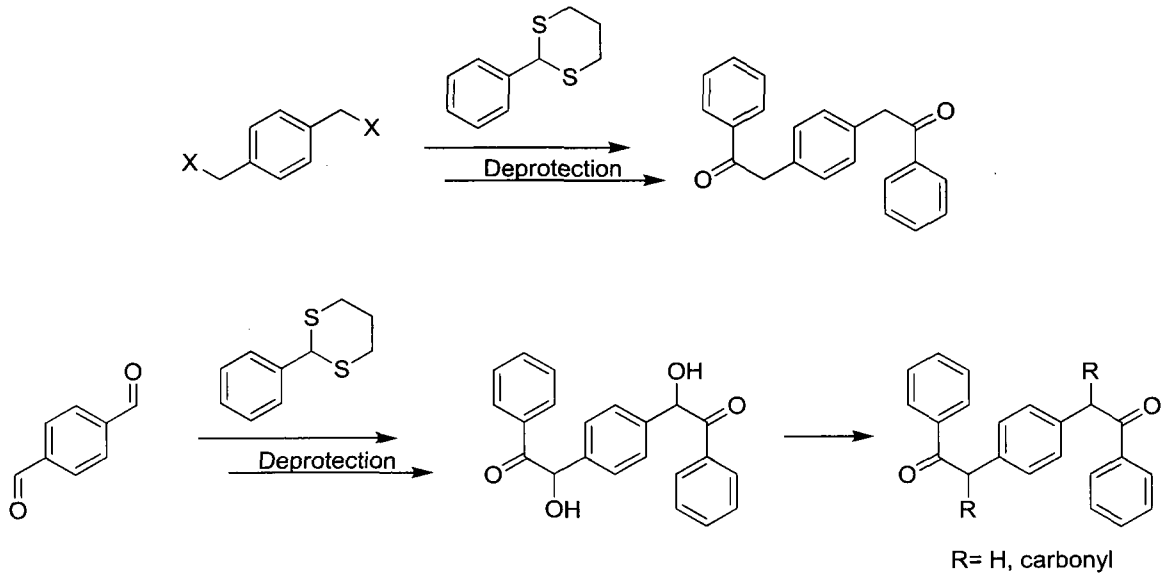
Scheme 12: Synthesis of 2-phenyl-1,3-dithiane (**6**) from benzaldehyde in DCM with catalytic $Hf(OTf)_4$.

With respect to synthetic application, 1,3-dithianes are preferred over bis(phenylthio)acetals. Though bis(phenylthio)acetals have been utilized in Umpolung reactions, the anion intermediate is less stable than that of the 1,3-dithiane. The bis(phenylthio)acetal requires *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) to stabilize the deprotonated anion intermediate.[66] Conversely 1,3-dithianes do not require an added stabilizer due to the polarizability of the sulfur moieties.

2.1.2.2. Utilization of Thioacetals

Due to the versatility of our synthetic strategy, the hub could contain either thioacetal or the electrophile moiety (**Figure 10**). Though both types of hub compounds were synthesized, we focused our effort on hubs that contained the electrophile. Thioacetals have been shown to react readily with both aryl halides as well as aldehydes.[54] Aryl bromides show more promise than their aldehyde counterparts for the

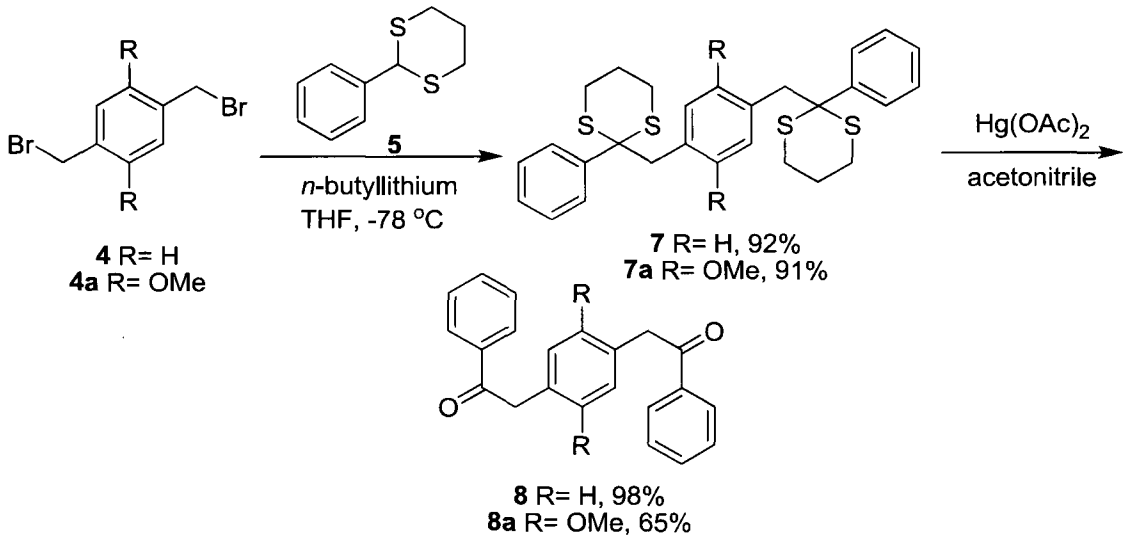
production of PAH compounds by reducing the number of steps required to obtain the desired framework (**Scheme 13**). It should be noted however, that the framework resulting from an aldehyde analog is unique, and through modification could afford equally interesting PAH products.



Scheme 13: comparison of alkyl halide and anldehyde hub product formation from an Umpolung reaction. Aldehydes require modification of Umpolung product to reach the same framework as is achieved in the alkyl halide Umpolung reaction.

With the desired hub compound containing electrophilic moieties and an appropriate thioacetal in place, an Umpolung reaction was optimized to afford products in 92% yield. *n*-Butylithium was used to deprotonate **5** at -78 °C in anhydrous tetrahydrofuran (THF) at which point the solution turned color from clear to dark green. At -78 °C, α,α'-dibromo-*p*-xylene (**4**) in THF was added drop wise over 5-10 minutes to the deprotonated **6** and the reaction was allowed to slowly warm to room temperature. Reaction progress could be monitored visually as the dark green color slowly faded to a

rosy pink suspension. The pink suspension persisted for a short time before finally yielding a milky white solution indicating the formation of 1,4-bis((2-phenyl-1,3-dithian-2-yl)methyl)benzene (**7**). Solvents were removed under reduced pressure yielding **7** as a white solid. The crude product proved to be pure with no indication of the monoadduct impurity (**Scheme 14**). It is theorized that the rosy pink suspension could be evidence of a less soluble monoadduct. This would indicate, as expected, that thioacetal addition to the hub happens sequentially, rather than simultaneously.



Scheme 14: Reaction between α,α′-dibromo-*p*-xylene (**4**) and dithiane (**6**) with subsequent deprotection of 1,4-bis((2-phenyl-1,3-dithian-2-yl)methyl)benzene (**7**) to afford diketone **8**.

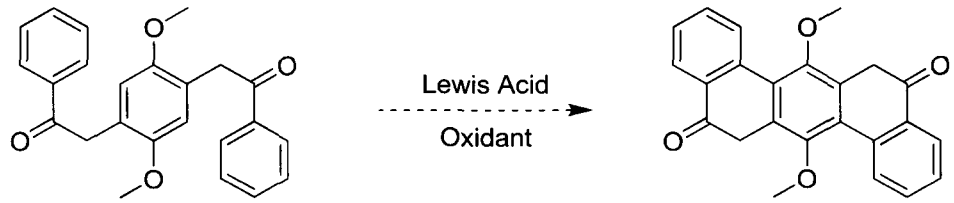
Thioacetal derivatives are, in general, cleaved by reaction with Hg(II) salts or by oxidation.[68] Deprotection of **6** was achieved by stirring in acetonitrile with mercuric(II) acetate [$Hg(OAc)_2$] for two hours, after which the solution was filtered through celite. The celite removed any mercuric by-products, however, copious amounts of DCM were necessary to extract 2,2'-(1,4-phenylene)bis(1-phenylethanone) (**8**) from the celite as **8**

suffers from poor solubility. Compounds **8** and **8a** were isolated as pale yellow solids in 98% and 65% yields respectively.

2.1.3. Scholl Chemistry

2.1.3.1 Non Aromatic Scholl Formation

The formation of PAH frameworks from oligophenylene derivatives has been accomplished using the Scholl reaction.[90-92] Though the majority of Scholl applications have been directed at reactions that yield aromatic framework, there are also literature precedents for the formation of non aromatic rings using Scholl conditions.[102-105] From these reports, it was postulated that **8a** would cyclize to form the carbon framework of the desired PAH (**Scheme 15**).



8a

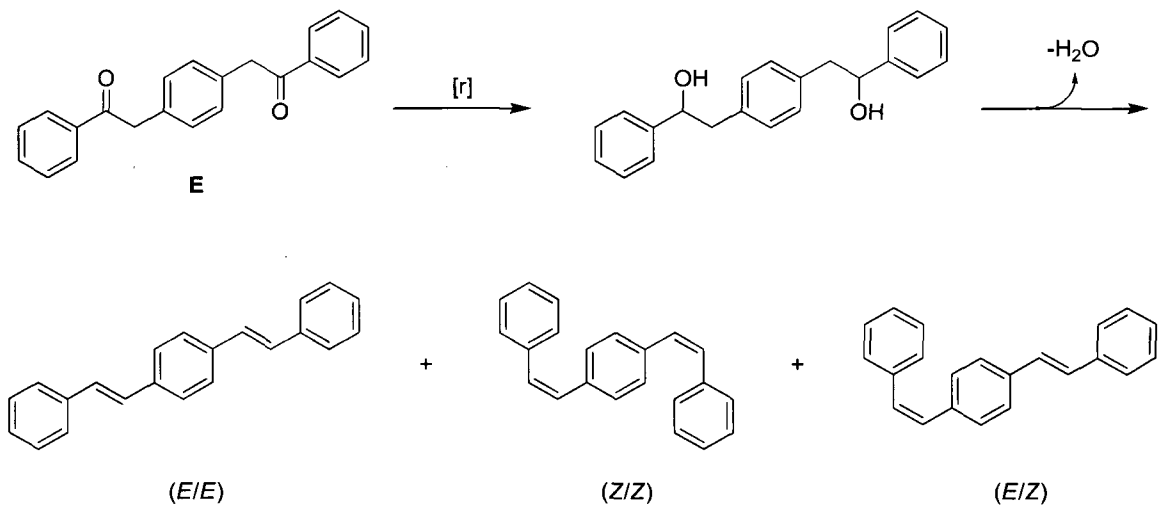
Scheme 15: Desired Scholl cyclization reaction on unmodified, deprotected umpolung product **8a**.

In an attempt to promote cyclization, **8a** was chosen over **8** as starting material for this reaction. The addition of electron donating methoxy groups has been shown to enhance the reactivity of Scholl reactions.[86] A variety of conditions were attempted to perform the cyclization including conditions from literature Scholl reactions resulting in

non-aromatic products. Reagents utilized included $(CF_3COO)_2I^{III}C_6H_5$ (PIFA) with $BF_3 \cdot Et_2O$ in DCM, which resulted in an unidentified insoluble material determined not to be the desired product. Additionally, 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) with $MeSO_3H$ in DCM and VOF_3, and $BF_3 \cdot Et_2O$ in DCM were utilized in separate reactions but they both gave only starting material. It was determined that implementation of the Scholl reaction may be premature at this stage of the synthesis. Although a few literature examples exist, the formation of a non-aromatic product lacks the thermodynamic driving force that may be critical for the successful Scholl reaction. It was thus determined that modification of the carbonyl moiety linking the benzene rings would be necessary. In particular, we sought to add unsaturation to the C-C skeleton such that subsequent Scholl cyclization would produce a fully aromatic product.

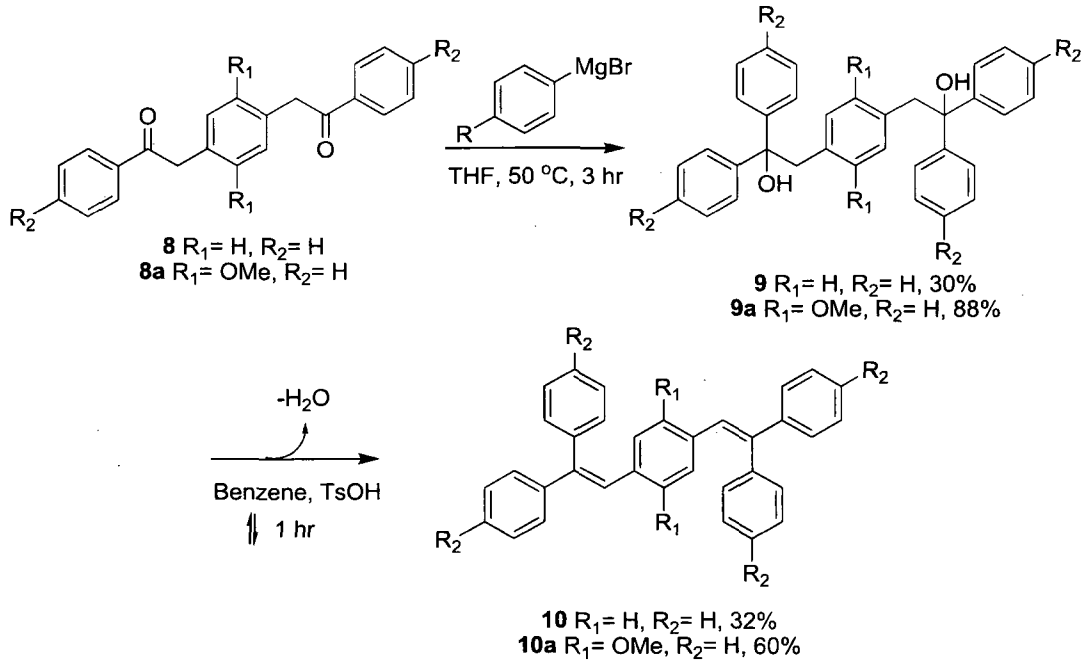
2.1.3.2 Grignard Reaction

In an attempt to remove any variables that could be hindering the Scholl reaction, modification of the two carbon linker between the aryl groups of **8a** and **8** was desired to ensure that a Scholl cyclization would yield a fully aromatic product. The reduction of the carbonyl functionality on **8** and **8a**, followed by dehydration would lead to the desired framework. However, this strategy is flawed due to the lack of selectivity in the final products of the newly formed double bonds (*E*/*E*)(*Z*/*Z*)(*E*/*Z*) (**Scheme 16**). For the Scholl reaction to take place the newly formed olefin must be in the *Z*/*Z* conformation.



Scheme 16: Reduction followed by dehydration 2,2'-(1,4-phenylene)bis(1-phenylethanone) (**8**) yielding a mixture of isomers. (Reactions not performed).

Due to the lack of a stereospecific reduction-dehydration sequence that would produce only the *Z*/*Z* product, an alternate method for the formation of the olefins was designed. It was determined that a Grignard addition of a phenyl group would eliminate the need for a stereospecific dehydration reaction, as bond rotation about the σ-bond α to the central benzene ring would ensure that one of the terminal phenyl groups would be properly positioned for the subsequent Scholl reaction (**Scheme 17**).



Scheme 17: Grignard addition of a phenylmagnesiumbromide to 2,2'-(1,4-phenylene)bis(1-phenylethanone) (**8**) followed by dehydration yielding1,4-bis(2,2-diphenylvinyl)benzene (**10**).

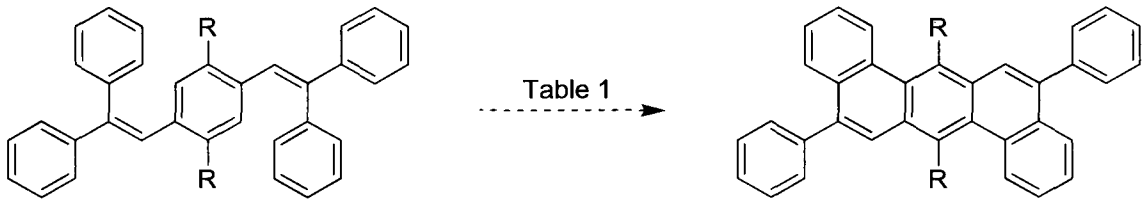
The utilization of a Grignard addition followed by subsequent dehydration proves to be dually beneficial. The proper framework introduced for Scholl ring closure, and an additional opportunity to functionalize the resulting PAH is presented. Functionalization is important as bare PAHs suffer from poor solubility. For simplicity, the starting thioacetal and the Grignard reagent should be identically substituted at R_2. It is necessary for each to be substituted identically in order to avoid a mixture of isomeric products in the dehydration step.

The addition of the phenylgrignard reagent was performed using known reaction conditions.[109, 110] The Grignard reaction (**Scheme 17**) yielded 2,2'-(1,4-phenylene)bis(1,1-diphenylethanol) (**9**) (30%) and 2,2'-(2,5-dimethoxy-1,4-phenylene)bis(1,1-diphenylethanol) (**9a**) (88%). Both **9** and **9a** are yellow powders. They were immediately

dehydrated in boiling benzene with *p*-toluenesulfonic acid to afford 1,4-bis(2,2-diphenylvinyl)benzene (**10**) (32%) and (2,2'-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1,1-triyl))tetrabenzene (**10a**) (60%) as neon green and neon yellow powders respectively. The reactions were repeated multiple times. In one experiment, the Grignard reaction gave **10a** directly with no need for dehydration. However, this was only observed once and because dehydration was performed relatively cleanly and easily, the direct conversion process was not optimized.

2.1.3.3. Aromatic Scholl reaction

The Scholl reaction was attempted using a number of conditions in an attempt to cyclize **10** and **10a** (**Table 1**). It was hoped that the existing framework leading to a fully aromatic compound would be significant enough to drive the reaction to completion (**Scheme 18**).



10 R= H
10a R=OMe

1 R= H
1a R=OMe

Scheme 18: Scholl reaction of 1,4-bis(2,2-diphenylvinyl)benzene (**10**).

Table 1: Conditions for attempted Scholl reaction of **10** and **10a**.

Lewis Acid	Oxidant	Solvent
$(CF_3COO)_2I^{III}C_6H_5$ (PIFA)	$BF_3{\cdot}Et_2O$	DCM
$MeSO_3H$	DDQ	DCM
VOF_3	$BF_3{\cdot}Et_2O$	DCM
$FeCl_3$	Nitromethane	DCM

As with the non-aromatic Scholl attempts, the inclusion of electron donating groups was seen as a benefit. As such, **10a** was the focus of early attempts at a Scholl cyclization. Though none of the conditions yielded the desired product, a one hour reaction with yielded what was thought to be a mono-cyclized Scholl product (**Figure 11**). As an undesired product of an incomplete reaction, the crude product was resubmitted to the same reaction conditions for 16 hours resulting in a black amorphous solid. The crude mono-Scholl product was characterized by ^{1}H NMR but never purified.

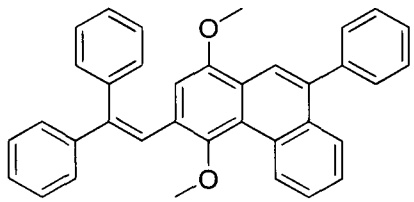
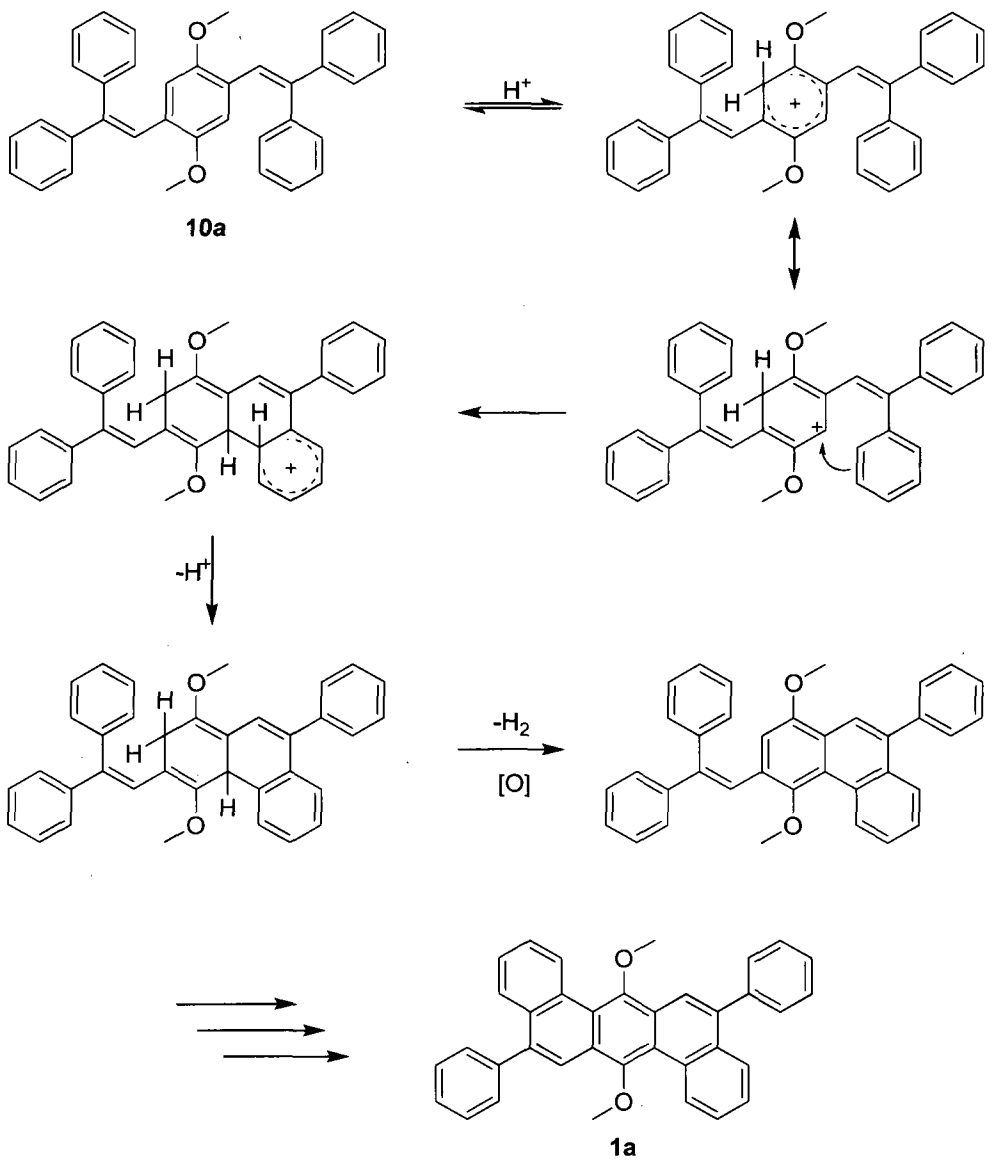


Figure 11: Mono-Scholl product observed in crude reaction workup, not fully characterized.

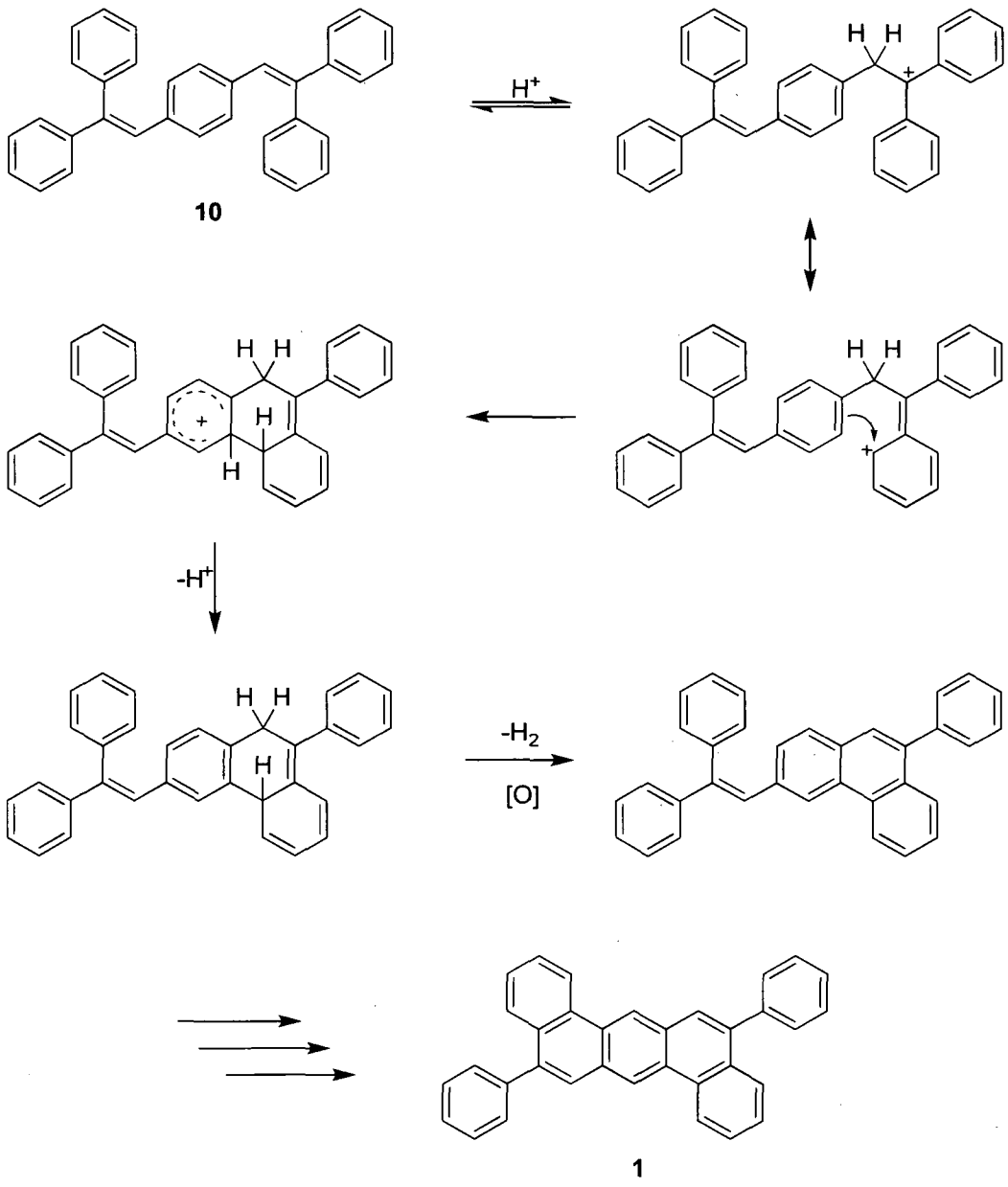
Assuming a mechanism analogous to that discussed by King and co-workers,[94] we anticipated Scholl cyclization as outlined in **Scheme 19**. thus, initial protonation at the methoxy substituted hub would produce a resonance delocalized cyclohexadienyl cation that can act as an electrophile in the first cyclization.



Scheme 19: Anticipated Scholl cyclization of **10a** to produce **1a**.

Following loss of a proton and air oxidation, the mono-Scholl product of **Figure 11** is produced. A second protonation-deprotonation-dehydrogenation sequence would produce the fully aromatic product **1a**.

While methoxy substitution on the central ring should have promoted the mechanism shown in **Scheme 19**, it was considered that unsubstituted **10** may also react under Scholl conditions, potentially via a unique mechanism as illustrated in **Scheme 20**. Thus, protonation at an alkenyl carbon alpha to the hub produces a resonance stabilized diphenyl methyl cation that can cyclize as shown.

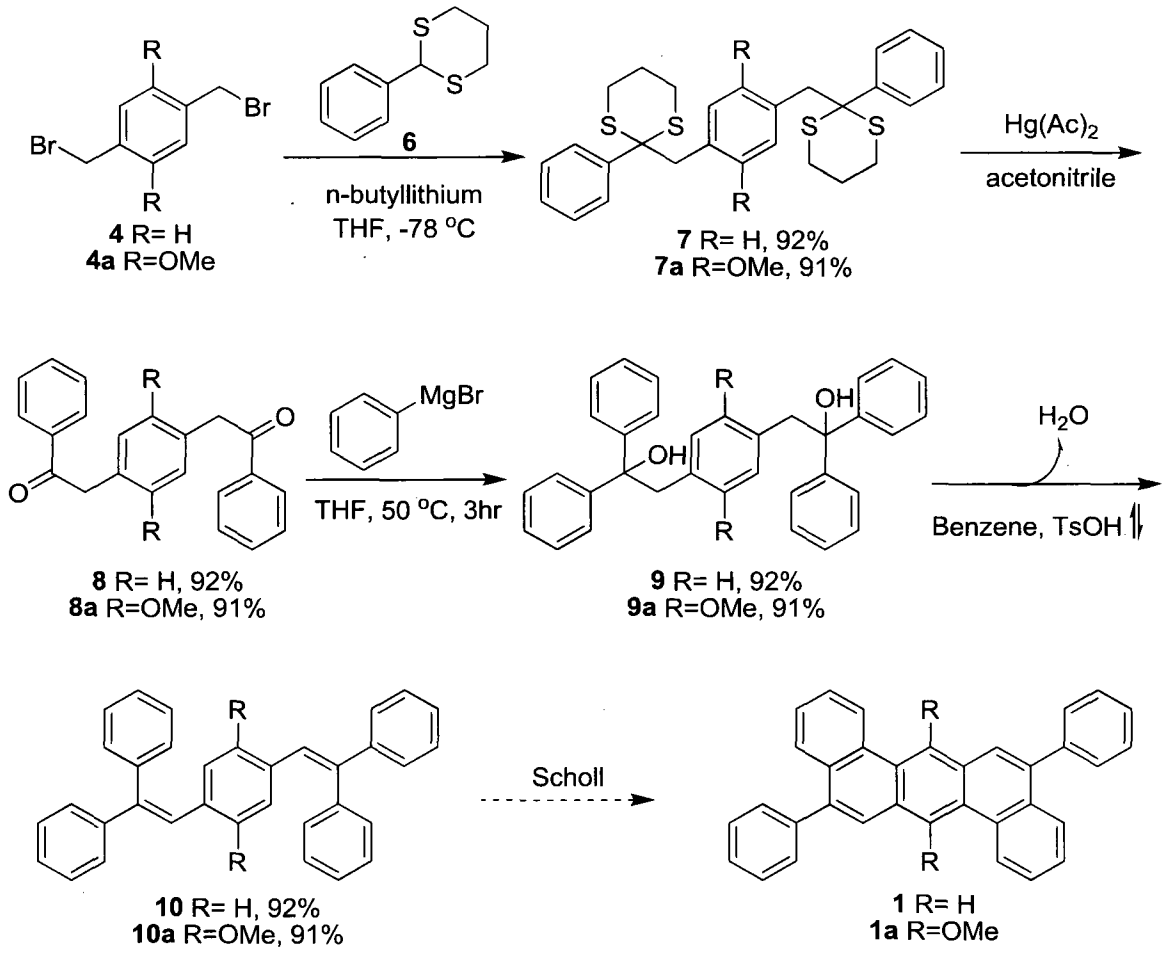


Scheme 20: Anticipated Scholl cyclization of **10** to produce **1**.

Despite our efforts there was no observation of product formation despite many variations in reaction conditions. Scholl conditions that yielded no products included those attempted on **8a**, $(CF_3COO)_2I^{III}C_6H_5$ (PIFA) with $BF_3 \cdot Et_2O$ in CH_2Cl_2, 2,3-Dichloro-5,6-Dicyanobenzoquinone (DDQ) with $MeSO_3H$ in CH_2Cl_2 and VOF_3/ $BF_3 \cdot Et_2O$ in CH_2Cl_2. In all cases, the reactions produced many products as evidence by broad "haystacking" in the aromatic region of the crude ^1H NMR spectra. Isolation of desired products was not achieved despite attempting a variety of column and prep-plate TLC solvent conditions. Pure solvents such as DCM, ethyl acetate (EtOAc), hexanes, benzene, and diethyl ether (Et_2O) were all tested via TLC as well countless mixtures of each. In all cases, the aromatic products co-eluted, and no isolated products were identified. It is necessary in this reaction to find reactive conditions which produce the product cleanly with no degradation of starting material and better or no by-product formation.

One final set of reagents, iron(III) trichloride with nitromethane in CH_2Cl_2, did yield a clean isolable PAH product. ^1H NMR spectra showed evidence for a fully aromatic species, however ^{13}C NMR spectra were inconclusive as the poor solubility of the product lead to poor signal to noise. Matrix-assisted laser desorption/ionization time of flight (MALDI TOF) mass spectra were not consistent with desired product **1**. The largest mass observed was 360, while the molecular weight of **1** is 406.

Although neither **1** nor **1a** were prepared, a general synthetic strategy was devised that could lead to a variety of PAH compounds as illustrated in **Scheme 21**. It is possible that the properties that inhibited formation of **1** could be avoided in other cases.

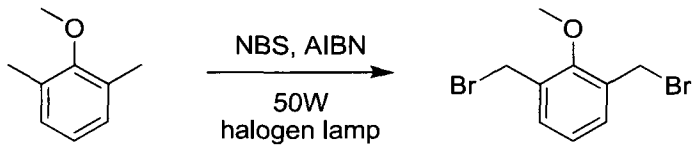


Scheme 21: Complete synthetic strategy for the formation of a novel PAH as designed for the formation of **1** and **1a**.

Further work will be required to find sutable conditions for the cyclization of **10** and **10a**. It may also be possible to effect the same reaction through alternative means like, e.g., the direct cyclization of diols **9** and **9a** via either Lewis or Brønstead acid catalysis.

2.2 Progress Towards 3,6-diphenyl-9-methoxydibenzo[a,h]anthracene (2)

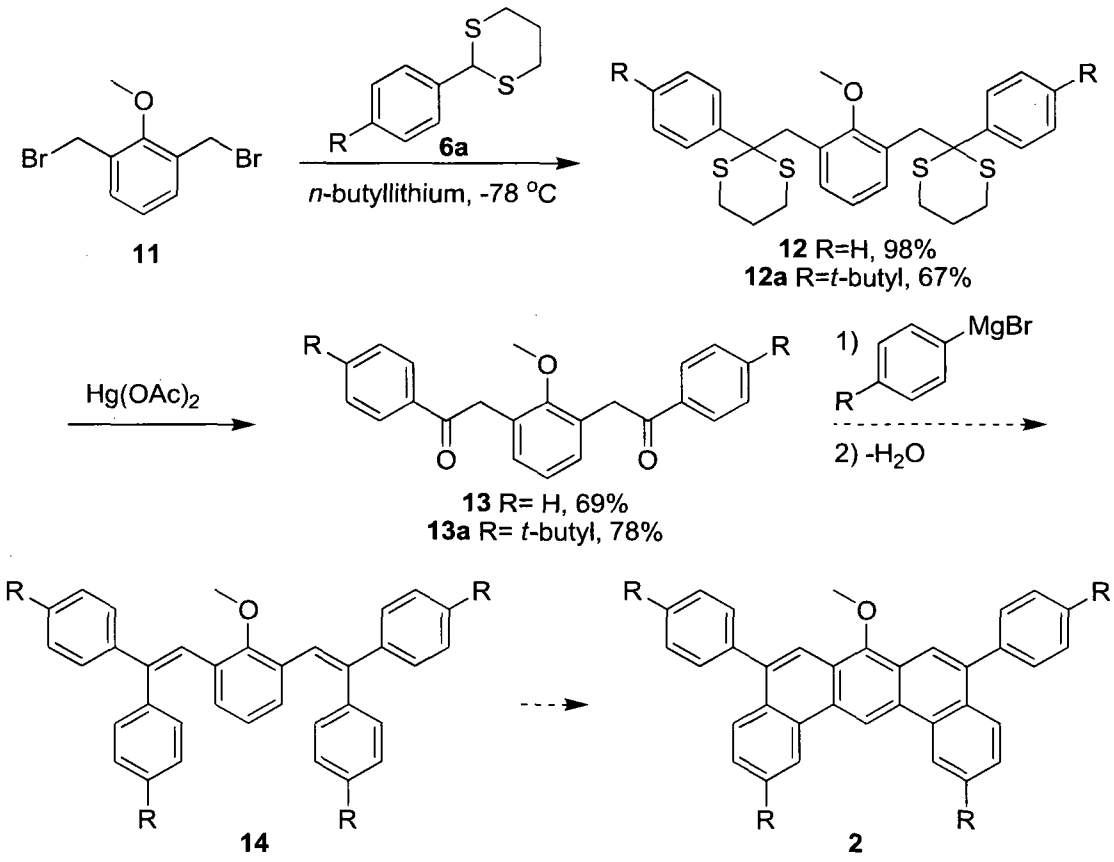
The proposed synthesis of 3,6-diphenyl-9-methoxydibenzo[a,h]anthracene (**2**) utilizes a *meta* substituted aromatic core or hub, 1,3-bis(bromomethyl)-2-methoxybenzene (**11**). Compound **11** was synthesized from commercially available vanaline by radical bromination. In a solution of chloroform, N-bromosucinimide (NBS) and vanaline were irradiated with a 50W halogen lamp light for 16 hours. Azobisisobutyronitrile (AIBN) was used to initiate the reaction producing **11** in 48% yield (**Scheme 22**).



11, 48%

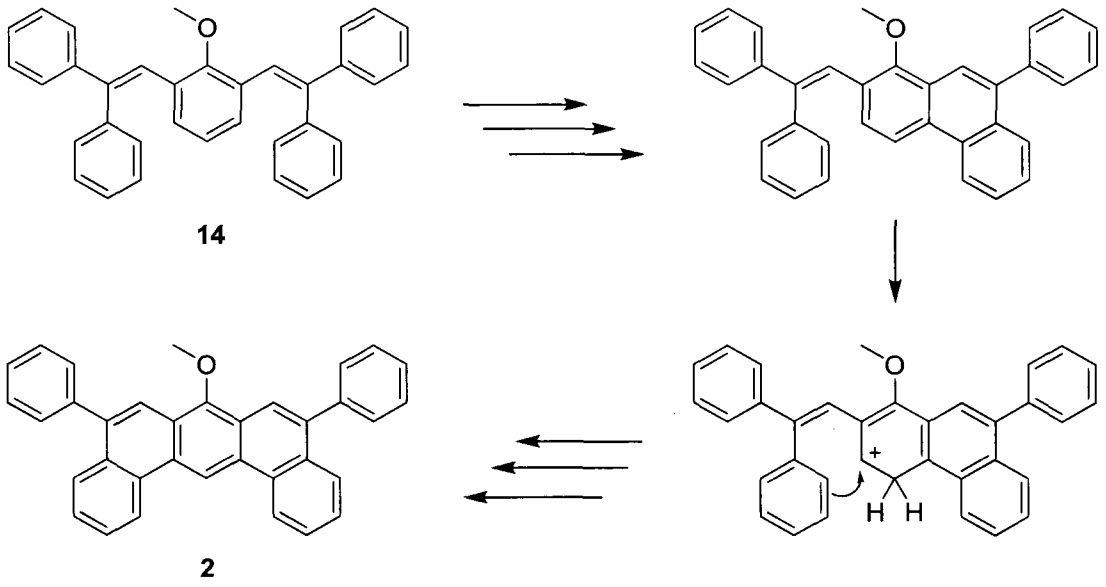
Scheme 22: Synthesis of 1,3-bis(bromomethyl)-2-methoxybenzene (**11**) from Vanaline.

From **11** the synthesis of **2** proceeded as illustrated in **Scheme 23**. Thus, deprotonation of 1,3-dithiane using *n*-butyllithium in THF solvent produces nucleophilic dithiolate anion that reacts twice with dibromobenzyl **11** to produce **12** and **12a** in 98% and 67% yields, respectively. Deprotection using mercuric acetate affords diketones **13** and **13a** in good yield.



Scheme 23: Synthetic sequence for the synthesis of 3,6-diphenyl-9-methoxydibenzo[a,h]anthracene (**2**).

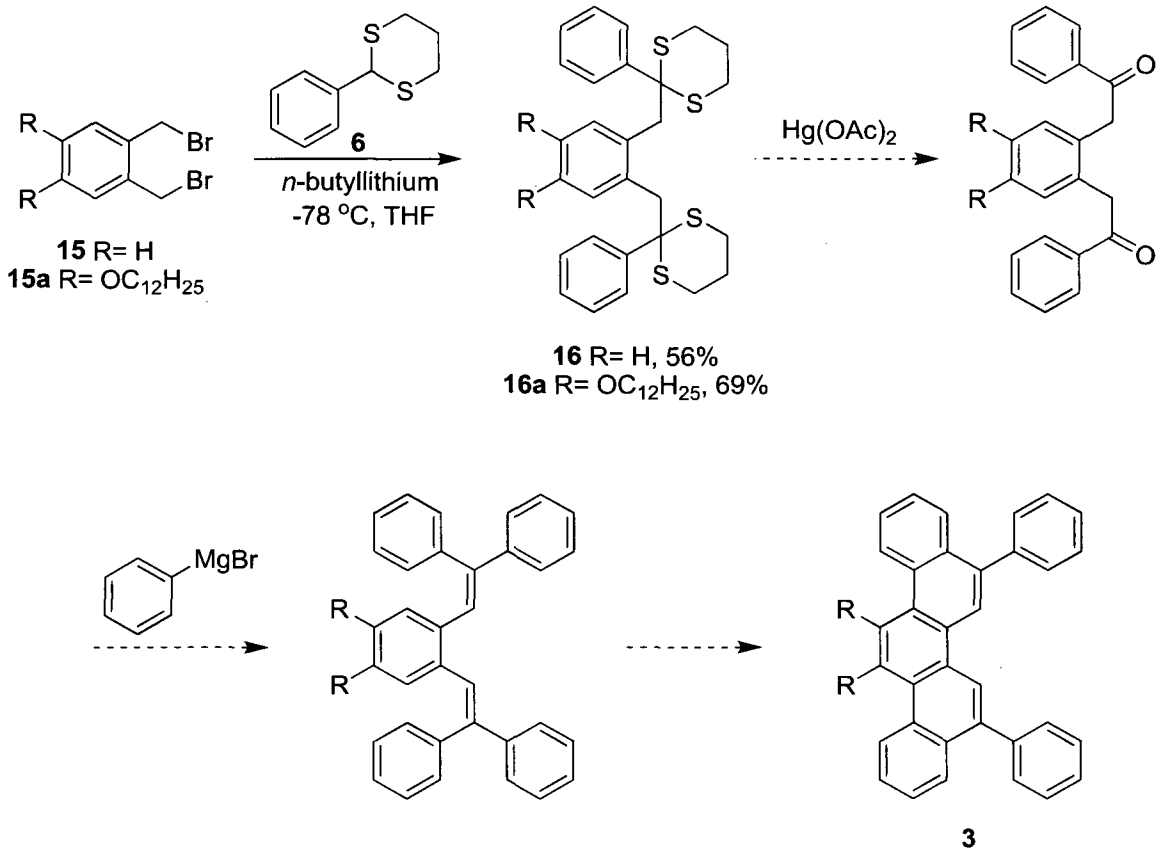
The Grignard addition of phenyl groups has not been performed at this time, though literature precedents suggest the reaction and subsequent dehydration should proceed smoothly. The Scholl cyclization of (2,2'-(2-methoxy-1,3-phenylene)bis(ethene-2,1,1-triyl))tetrabenzene (**14**) should begin with protonation at the hub carbon that is situated *para* to the methoxy group. The resulting cyclohexadienyl cation is extensively delocalized and should cyclize to form a phenanthrene intermediate as illustrated in **Scheme 24**. A second cyclization of this intermediate should produce the desired dibenzo[a,h]anthracene derivative **2**.



Scheme 24: Proposed Scholl reaction of **14**.

2.3. Progress Towards A phenyl substituted picene (3)

The final PAH resulting from an *ortho* substituted benzene hub is be a substituted picene. Because picene maps directly onto grapheme and arm-chair carbon nanotubes, it is a highly desired compound for organic electronic applications.[106] Compound **15** with *ortho* dibromomethyl groups was reacted with nucleophilic dithiolate anion to produce **16** and **16a** in good yield as illustrated in **Scheme 25**.



Scheme 25: Synthetic sequence for the synthesis of a phenyl substituted picene (**3**)

In an attempt to make a PAH with greater solubility, the utilization of a 1,2-bis(bromomethyl)-4,5-bis(dodecyloxy)benzene (**15**) hub obtained from Mikael Jazdzyk. However, as reported earlier this is no longer an acceptable approach as the Scholl step will most likely be problematic. Regardless, the bare hub would yield an interesting compound, and the addition of two phenyls should give picene adequate solubility.

2.4. Conclusions

The synthesis and functionalization of angular benzo fused anthracenes **1** and **2** and picene **3** derivatives have been attempted utilizing a unique synthetic strategy. Functionalization of these PAHs can be utilized to effect solubility, electronic properties, as well as the stability (i.e., photooxidative and photodimerization resistance) of each. In the pursuit of compounds **1**, **2** and **3**, new synthetic strategies have been devised. Here we report for the first time the utilization of reverse polarity chemistries (i.e. Umpolung) to form a variety of PAH derivatives using a versatile reaction scheme.

Reaction of bromomethylbenzene derivatives **4**, **11** or **15** with 1,3-dithiane **6** followed by deprotection of the thioacetal moiety yields carbonyl products with carbon frameworks that map directly onto **1**, **2**, or **3**. Subsequent Grignard addition and dehydration produced **10** which can potentially be converted to PAH **1**. Though Scholl cyclization reactions were attempted, the conversion of **10** and **10a** to **1** and **1a** respectively, was not observed. It is hoped that dehydrated Grignard products resulting from *meta* and *ortho* bromomethylbenzene derivatives **11** and **15** may be more amenable to Scholl cyclization. An alternative approach to cyclization involves formation of a diol species **8** after Grignard addition to the carbonyl intermediates **8** and **13**. Acid catalyzed dehydration to form a dibenzyl stabilized carbocation capable of electrophilic aromatic substitution may be a more effective route.

By design, our proposed syntheses allow a variety of opportunities to vary substitution patterns of each targeted PAH. The central aromatic cores (**4**, **11**, and **15**), the thioacetal moiety (**6**), the Grignard moiety, and carbonyl intermediates (**8** and **13**) can all

be readily modified making the synthetic scheme a versatile approach towards PAH synthesis.

2.5. Experimental

2.5.1. General Methods

^{1}H NMR spectra (^{1}H NMR) were obtained on a Varian INOVA 500 FT-NMR operating at 499.776 MHz and a Varian Mercury Plus 400 FT-NMR operating at 399.751 MHz. All chemical shift (δ_H) values are reported in parts per million (ppm) relative to Me_4Si (TMS).

^{13}C NMR spectra (^{13}C NMR) were obtained on a Varian INOVA 500 FT-NMR operating at 124.626 MHz and a Varian Mercury Plus 400 FT-NMR operating at 100.517 MHz. All chemical shift (δ_H) values are reported in parts per million (ppm) relative to Me_4Si (TMS).

Mass Spectra were obtained on a Kratos Axima-CFR Laser Desorption-Time Of Flight Mass Spectrometer.

2.5.2. Solvents

Note: All solvents were not purified further unless otherwise noted.

Acetic acid (CH_3CO_2H) was obtained from VWR Chemical Co.

Benzene (C_6H_6) was obtained from EM Science.

Chloroform ($CHCl_3$) was obtained from EM Science.

Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories.

Dichloromethane (CH_2Cl_2) was obtained from EM Science.

Ethyl Acetate ($C_4H_8O_2$) was obtained from EM Science.

Hydrochloric Acid (HCl) was obtained from EM Science.

Methanol (CH_4O) was obtained from EMD Chemicals.

Tetrahydrofuran (C_4H_8O) was obtained from EM Science, and was dried over sodium prior to use.

2.5.3. Chromatography

Sea Sand was obtained from VWR Scientific Products.

Silica Gel (38-75 μm Flash Chromatography Packing) was obtained from Natland International Co.

2.5.4. Reagents

Anisole (C_7H_8O) was obtained from Aldrich Chemical Co.

Azobisisobutyronitrile (AIBN) was obtained from Aldrich Chemical Co.

Benzaldehyde (C_7H_6O) was obtained from EM Science.

N-Bromosuccinimide (NBS) was obtained from Aldrich Chemical Co.

p-tert-Butylbenzaldehyde ($C_{11}H_{14}O$) was obtained from Aldrich Chemical Co.

n-Butyllithium (C_4H_9Li) was obtained from Alfa Aesar Chemical Co.

Calcium chloride ($CaCl_2$) was obtained from Fisher Scientific Co.

α,α′-Dibromo-*p*-xylene ($C_8H_8Br_2$) was obtained from Aldrich Chemical Co.

Hafnium trifluoromethanesulonate [$Hf(OTf)_4$] was obtained from Alfa Aesar Chemical Co.

Hydrobromic acid 33% AcOH (HBr) was obtained from EM Science.

Hydrochloric acid (HCl) was obtained from EM Science.

Mercuric(II) acetate [$Hg(OAc)_2$] was obtained from J. T. Baker Co.

p-Methoxybenzene ($C_8H_{10}O_2$) was obtained from Aldrich Chemical Co.

Paraformaldehyde [$OH(CH_2O)_nH$] was obtained from Aldrich Chemical Co.

Phenylmagnesium bromide (C_6H_5MgBr) was obtained from Aldrich Chemical Co.

1,3-Propanedithiol ($C_3H_8S_2$) was obtained from Alfa Aesar Chemical Co.

Sodium bisulfite ($NaHSO_3$) was obtained from EM Science.

p-Toluenesulfonic acid ($CH_3C_6H_4SO_3H$) was obtained from Aldrich Chemical Co.

2.5.5. Synthesis

α,α′-Dibromo-2,5-dimethoxy-*p*-xylene (4a). In a 500 mL round-bottomed flask, paraformaldehyde (3.5g, 117 mmol) and *p*-methoxybenzene (5g, 36.2 mmol) were added to acetic acid (AcOH)(131 mL) to give a colorlesssuspension. The reaction was heated to 80 °C, hydrobromic acid 33% AcOH (13.1 mL, 80 mmol) was added. The reaction was stirred under N_2 for 3 hours resulting in a white powder. The reaction was kept at 5 °C overnight then filtered through a glass frit and washed with excess water to yield pure 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (7.07 g, 21.82 mmol, 60.3 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 6H), 4.55 (s, 4H), 6.89 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.62, 56.20, 114.54, 127.43, 151.27.

1,2-bis(bis(Phenylthio)methyl)benzene (5). A 50 mL round bottomed flask was charged with thiophenol (10 mL, 97 mmol), anhydrous $CaCl_2$ (1.9 g, 17.2 mmol) and 5 drops of conc. HCl. The solution was cooled to 0 °C in an ice bath. Phthalaldehyde (0.5 g, 3.7 mmol) was added to the reaction flask. The resulting mixture was refluxed

vigorously for 5-10 minutes and was allowed to stand at room temperature over night. The reaction mixture was diluted with distilled water (20 mL) and extracted with ether (3 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed under reduced pressure, yielding 1,2-bis(bis(phenylthio)methyl)benzene (1.39 g) 81% yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.02 (s, 2H), 7.19-7.24 (m, 12H), 7.25-7.27 (m, 10H), 7.59 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.22, 127.82, 128.18, 128.85, 132.50, 134.15, 135.59.

2-Phenyl-1,3-dithiane (6). A 200 mLround bottomed flask was charged with 1,3-propanedithiol (4.92 mL, 49.0 mmol), benzaldehyde (5 mL, 49.0 mmol) and dichloromethane (DCM) (49.0 mL) to give a colorlesssolution. Hafnium trifluoromethanesulfonate [$Hf(OTf)_4$] (0.038 g, 0.049 mmol) was added, and the solution stirred for 4 hours. The reaction was flushed through a cake of silica and dried over $CaCl_2$ and concentrated under reduced pressure to yield a clear oil. Methanol was added and the solution was briefly sonicated producing a white precipitate. The suspension was cooled to 0 °C for 1 hour and the solvent was removed via filtration to produce pure 2-phenyl-1,3-dithiane (6.5g) 67% yield. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.89-2.01 (m, 1H), 2.15-2.22 (m, 1H), 2.89-2.95 (m, 2H), 3.04-3.12 (m, 2H), 5.18 (s, 1H), 7.27-7.37 (m, 3H), 7.45-7.48 (m 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.15, 32.13, 51.52, 127.79, 128.47, 128.76, 139.13.

2-(4-tert-Butylphenyl)-1,3-dithiane (6a). In a 200 mL round bottomed flask, 1,3-propanedithiol (3.02 mL, 29.9 mmol) and *p-tert*-butylbenzaldehyde (5 mL, 29.9 mmol) were added to DCM (59.0 mL) to give a colorless solution. Hafnium

trifluoromethanesulfonate ($Hf(OTf)_4$) (0.021 g, 0.03 mmol) was added and the solution allowed to stir for 4hr. The solution was filtered through a cake of silica and dried over $CaCl_2$ and concentrated under reduced pressure to yield 2-(4-tert-butylphenyl)-1,3-dithiane as a white solid (5.4 g, 21.39 mmol, 71.6 % yield) . ^1H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, CH_3, 9H), 1.87-2.00 (m, 1H), 2.17-2.20 (m, 1H), 2.89-2.95 (m, 2H), 3.02-3.10 (m, 2H), 5.19 (s, 1H), 7.31-7.40 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.15, 31.27, 32.17, 34.60, 51.14, 125.69, 127.35, 136.04, 151.39.

1,4-bis((2-Phenyl-1,3-dithian-2-yl)methyl)benzene (7). In a 250 mL round-bottomed flask2-phenyl-1,3-dithiane (2.08 g, 10.59 mmol) was added to tetrahydrofuran (THF) (150 mL) to give a colorlesssolution. The reaction was cooled to -78 °C and n-Butyllithium 2.5 M in hexanes (5.09 mL, 12.71 mmol) was added drop-wise to give an orange solution. The reaction was kept at -78 °C for 30 minutes, then warmed to room temp for 30 minutes. The reaction was then cooled back to -78 °C and α,α'-dibromo-*p*-xylene (1.398 g, 5.30 mmol) in 3 mL dry THF was added to the solution drop-wise over 2 minutes. The reaction was allowed to warm to room temp over 30 minutes and was stirred at room temp for 3.5 hours. The reaction was then quenched with 30 mL of water and the phases separated in a separatory funnel. The aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20 mL) then 20 mL brine followed by drying over $CaCl_2$. The solvent was removed under reduced pressure to yield 1,4-bis((2-phenyl-1,3-dithian-2-yl)methyl)benzene (2.4 g, 4.85 mmol, 92 % crude yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.88-1.96 (m, 4H), 2.60-2.64 (m, 8H), 3.18 (s, 4H), 6.44 (s, 4H), 7.19-7.23 (m, 2H), 7.26-7.30 (m, 4H), 7.64-7.67 (m 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.06, 27.51, 51.19, 59.68, 126.89, 128.19, 129.48, 129.89, 132.84, 140.46.

2,2'-(2,5-Dimethoxy-1,4-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (7a). In a 250 mLround-bottomed flask 2-phenyl-1,3-dithiane (8 g, 40.7 mmol) was added to tetrahydrofuran (THF) (150 mL) to give a colorless solution. The reaction was cooled to -78 °C and n-butyllithium 2.5 M in hexanes (19.56 mL, 48.9 mmol) was added drop-wise to give an orangesolution. The reaction was kept at -78 °C for 30 minutes then warmed to room temp over 30 minutes. The reaction was then cooled back to -78 °C and α,α'-dibromo-2,5-dimethoxy-*p*-xylene (6.6 g, 20.37 mmol) in 3 mL dry THF was added drop-wise over 2 minutes. The reaction was allowed to warm to room temp over 30 minutes and was stirred at room temp for 3.5 hours. The reaction was quenched with 30 mL water. The organic phase was removed and the aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20 mL) then 20 mL brine then dried over $CaCl_2$. The solvent was removed under reduced pressure to yield 2,2'-(2,5-dimethoxy-1,4-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (10.3 g, 18.56 mmol, 91 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.88-1.96 (m, 4H), 2.60-2.64 (m, 8H), 3.18 (s, 4H), 3.25 (s, 4H), 5.89 (s, 2H), 7.15- 7.20 (m, 2H), 7.26-7.30 (m, 4H), 7.64-7.67 (m 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.15, 27.65, 43.90, 55.24, 60.25, 114.76, 122.23, 126.62, 128.03, 129.69, 140.91, 150.74.

2,2'-(1,4-Phenylene)bis(1-phenylethanone) (8). In a 50 mLround-bottomed flask, 1,4-bis((2-phenyl-1,3-dithian-2-yl)methyl)benzene (1.2 g, 2.425 mmol) was added followed by mercuric acetate (4.64 g, 14.55 mmol) in acetonitrile (34.6 mL) and water (5.77 mL)

to give a whitesuspension. The reaction was allowed to stir for 2 h at room temperature under nitrogen. The reaction was then diluted with 25 mL DCM and allowed to stir for 30 minutes, then filtered through a cake of silica. The silica was then washed with copious amounts of DCM and dried over $CaCl_2$. The solvent was removed under reduced pressure to afford 2,2'-(1,4-phenylene)bis(1-phenylethanone) (0.75 g, 2.386 mmol, 98 % yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.25 (s, 4H), 7.23 (s, 4H), 7.44- 7.48 (m, 4H), 7.53- 7.58 (m, 2H), 7.99- 8.02 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 45.09, 128.64, 128.68, 129.82, 133.16, 133.21, 136.61, 197.59.

2,2'-(2,5-Dimethoxy-1,4-phenylene)bis(1-phenylethanone) (8a). In a 50 mLround-bottomed flask2,2'-(2,5-dimethoxy-1,4-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (1.16 g, 2.09 mmol) was added followed by mercuric acetate (6.66 g, 20.91 mmol) in acetonitrile (30.5 mL) and water (4.3 mL) to give a white suspension. The reaction was allowed to stir for 2 hours at room temperature under nitrogen. The reaction was filtered through a cake of silica. The silica was then washed with copious amounts of DCM and dried over $CaCl_2$. The solvent was removed under reduced pressure to reveal 2,2'-(2,5-dimethoxy-1,4-phenylene)bis(1-phenylethanone) (0.51 g, 1.36 mmol, 65 % yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.72 (s, 6H), 4.25 (s, 4H), 6.78 (s, 2H), 7.41- 7.46 (m, 4H), 7.53- 7.58 (m, 2H), 8.05- 8.09 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.80, 56.12, 113.96, 122.98, 128.53, 128.54, 133.00, 136.88, 151.03, 198.11.

1,4-bis(2,2-Diphenylvinyl)benzene (10). In a 50 mL round-bottomed flask 2,2'-(1,4-phenylene)bis(1-phenylethanone) (1.1 g, 3.50 mmol) was added to dry THF (50 mL) to give a white suspension. The reaction was cooled to 0 °C and phenymagnesiumbromide

2.5 M in THF (11.20 mL, 28.0 mmol) was added drop-wise to give an orange solution. The reaction was stirred at 0 °C for 30 minutes then 50 °C for 3 hours. The reaction was quenched with water (20 mL) then diluted with 20 mL 1.5 M HCl. The organic layer was removed and the aqueous layer was extracted with (3 x 20 mL) DCM. The combined organics were washed with water (2 x 20 mL) then brine (20 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure to afford a red oil. The crude product was added to a silica gelcolumn and was eluted with DCM (to remove impurities) followed by ethyl acetate (EtOAc). The EtOAc fraction was collected and the solvent removed under reduced pressure to yield 2,2'-(1,4-phenylene)bis(1,1-diphenylethanol) (**9**) (0.5 g, 1.062 mmol, 30.4 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (s, 4H), 3.65-3.75 (m, 2H), 6.66 (s, 4H), 7.18- 7.24 (m, 4H), 7.25- 7.31 (m, 8H), 7.34- 7.38 (m, 8H). In a 250 mL round-bottomed flask *p*-Toluenesulfonic acid monohydrate (2.02 mg, 0.10 mmol) and 2,2'-(1,4-phenylene)bis(1,1-diphenylethanol) (0.5 g, 1.1 mmol) was added tobenzene (75 mL to give a green solution. The solution was refluxed under nitrogen with stirring for 1.5 hours. The reaction was washed with water (20 mL). The organic layer was removed and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20 mL) then brine (20 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure. The crude product was purified on a silica gel column and was eluted with DCM via gravity (R_f 0.86) to yield 1,4-bis(2,2-diphenylvinyl)benzene (0.150 g, 0.345 mmol, 32.5 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.79 (s, 4H), 6.86 (s, 2H), 7.16- 7.19 (m, 4H), 7.26- 7.30 (m, 8H), 7.30- 7.33 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.47, 127.50, 127.62, 127.90, 128.20, 128.65, 129.16, 130.39, 135.91, 140.39, 142.52, 143.49.

(2,2'-(2,5-Dimethoxy-1,4-phenylene)bis(ethene-2,1,1-triyl))tetrabenzene) (10a). In a 50 mLround-bottomed flask,2,2'-(1,4-phenylene)bis(1-phenylethanone) (0.2 g, 0.5 mmol was added to dry THF (15 mL) to give a white suspension. The reaction was cooled to 0 °C and phenymagnesiumbromide 2.5 M in THF (2.13 mL, 5.34 mmol) was added dropwise to give an orangesolution. The reaction was stirred at 0 °C for 30 minutes then at 50 °C for 3 hours. The reaction was quenched with water (20 mL) then diluted with 20 mL 1.5 M HCl. The organic layer was removed and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20mL) then brine (20 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure to reveal a yellow solid. 2,2'-(2,5-dimethoxy-1,4-phenylene)bis(1,1-diphenylethanol) (**9a**) (0.25 g, 0.47 mmol, 88 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.31 (s, 6H), 3.59 (s, 4H), 3.95 (s, 2H), 5.79 (s, 2H), 7.17- 7.22 (m, 4H), 7.25- 7.31 (m, 8H), 7.35- 7.39 (m, 8H). In a 250 mLround-bottomed flask, *p*-toluenesulfonic acid monohydrate (0.01g, 0.06 mmol) and 2,2'-(2,5-dimethoxy-1,4-phenylene)bis(1,1-diphenylethanol) (0.8 g, 0.2 mmol) were added to benzene (3 mL) to give a green solution. The solution was refluxed with stirring under nitrogen for 1.5 hours. The reaction was quenched with water (20 mL). The organic layer was removed and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organics were washed with water (2 x 10 mL) then brine (10 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure. The crude product was added to a silica gel column and was eluted with DCM via gravity (R_f= 0.9) to afford (2,2'-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1,1-triyl))tetrabenzene (0.045 g, 0.091 mmol, 60 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.20 (s, 6H), 6.23 (s, 2H), 7.11 (s, 2H), 7.22- 7.37 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.27, 112.32,

122.38, 125.52, 127.26, 127.35, 127.72, 128.11, 128.70, 130.55, 141.03, 142.28, 143.50, 151.03.

1,3-bis(Bromomethyl)-2-methoxybenzene (11). In a 500 mLround-bottomed flaskanisole (5mL, 38.2 mmol) and N-bromosuccinimide (14.95 g, 84 mmol) were added to $CHCl_3$ (382 mL) to give a colorlessAzobisisobutyronitrile (AIBN) (0.063 g, 0.382 mmol) was added, and the solution brought to reflux under N_2. The reaction was refluxed for 16 hours. The reaction was washed with a saturated solution of sodium bisulfite and 30 mL hot water. The organics were then dried over $CaCl_2$ and solvent removed under reduced pressure. The resulting oil was cooled to 5 °C and white crystals formed. The crystals were filtered and washed with cold methanol to yield α,α'-bromomethyl vanalin (5.4 g, 18.37 mmol, 48.1 % yield) as a white flaky solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.05 (s, CH_3, 3H), 4.59 (s, CH_2, 4H), 7.11 (t, 1H) J^3=X, 7.39 (d, 2H) J^3=X. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.49, 26.62, 125.09, 131.96, 132.25, 156.59.

2,2'-(2-Methoxy-1,3-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (12). In a 250 mL round-bottomed flask 2-phenyl-1,3-dithiane (1.87 g, 9.52 mmol) in THF (150 mL) was added to give a colorless solution. The reaction was cooled to -78 °C and n-butyllithium 2.5 M in hexanes (4.76 mL, 11.91 mmol) was added dropwise to give an orange The reaction was kept at -78 °C for 30 minutes then warmed to room temp for 30 minutes. The reaction was then cooled back to -78 °C and 1,3-bis(bromomethyl)-2-methoxybenzene (1.4 g, 4.75 mmol) in 10 mL dry THF was added dropwise over 2

minutes. The reaction was allowed to warm to room temp over 30 minutes and stirred at room temp for 3.5 hours. The reaction was quenched with 30 mL water and separated. The aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20 mL) then 20 mL brine then dried over $CaCl_2$. The solvent was removed under reduced pressure to yield 2,2'-(2-methoxy-1,3-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (2.45 g, 4.67 mmol, 98 % crude yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85-1.93 (m, 4H), 2.60-2.64 (m, 8H), 3.33 (s, 4H), 3.55 (s, 3H), 6.40-6.50 (m, 3H), 7.19-7.21 (m, 2H), 7.26-7.30 (m, 4H) 7.73- 7.78 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.85, 27.76, 44.14, 60.19, 61.68, 121.77, 126.76, 127.92, 128.20, 129.50, 131.41, 144.16, 158.51.

2,2'-(2-Methoxy-1,3-phenylene)bis(methylene)bis(2-(4-tert-butylphenyl)-1,3-dithiane) (12a). In a 250 mLround-bottomed flask 2-(4-tert-butylphenyl)-1,3-dithiane (1.54 g, 6.10 mmol) in THF (150 mL) was added to give a colorless The reaction was cooled to -78 °C and n-butyllithium 2.5 M in hexanes (3.05 mL, 7.63 mmol) was added dropwise to give an orange The reaction was kept at -78 °C for 30 minutes then warmed to room temp for 30 minutes. The reaction was then cooled back to -78 °C and 1,3-bis(bromomethyl)-2-methoxybenzene (0.89 g, 3.05 mmol) in 6 mL dry THF was added dropwise over 2 minutes. The reaction was allowed to warm to room temp over 30 minutes and stirred at room temp for 3.5 hours. The reaction was quenched with 30 mL water and separated. The aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20 mL) then 20 mL brine then dried over $CaCl_2$. The solvent was removed under reduced pressure to yield 2,2'-(2-methoxy-1,3-phenylene)bis(methylene)bis(2-(4-tert-butylphenyl)-1,3-dithiane) (1.3 g, 2.0 mmol,

67 % crude yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, CH_3, 18H) 1.85-1.93 (m, 4H), 2.60-2.64 (m, 8H), 3.33 (s, 4H), 3.50 (s, 3H), 6.39-6.43 (m, 3H), 7.22-7.24 (m, 4H), 7.63-7.65 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.96, 27.84, 31.39, 34.40, 44.19, 60.05, 61.70, 121.67, 125.06, 128.14, 129.07, 131.36, 138.36, 149.80, 158.51.

2,2'-(2-Methoxy-1,3-phenylene)bis(1-phenylethanone) (13). To a 50 mLround-bottomed flask,2,2'-(2-methoxy-1,3-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (0.46 g, 0.87 mmol) was added followed by mercuric acetate (1.67 g, 5.26 mmol) in acetonitrile (12.5 mL) and water (2.0 mL) to give a white The reaction was allowed to stir for 2 hours at room temperature under nitrogen. The reaction was diluted with 20 mL DCM and allowed to stir for 30 minutes, then filtered through a cake of silica. The silica was then washed with copious amounts of DCM and dried over $CaCl_2$. The solvent was removed under reduced pressure to reveal 2,2'-(2-methoxy-1,3-phenylene)bis(1-phenylethanone) (0.21 g, 0.61 mmol, 69 % yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.62 (s, 3H), 4.39 (s, 3H) 6.69- 7.15 (m, 3H), 7.41- 7.43 (m, 4H), 7.51- 7.59 (m, 2H), 8.00- 8.02 (m, 4H).

2,2'-(2-Methoxy-1,3-phenylene)bis(1-(4-tert-butylphenyl)ethanone) (13a). In a 50 mL round-bottomed flask2,2'-(2-methoxy-1,3-phenylene)bis(methylene)bis(2-(4-tert-butylphenyl)-1,3-dithiane) (0.8 g, 0.1 mmol) was added followed by mercuric acetate (0.24 g, 0.75 mmol) in acetonitrile (1.79 mL) and water (0.29 mL) to give a white The reaction was allowed to stir for 2 hours at room temperature under nitrogen. The reaction was diluted with 10 mL DCM and allowed to stir for 30 minutes, then filtered through a cake of silica. The silica was then washed with copious amounts of DCM and dried over

$CaCl_2$. The solvent was removed under reduced pressure to reveal 2,2'-(2-methoxy-1,3-phenylene)bis(1-(4-tert-butylphenyl)ethanone) (0.45 g, 0.099 mmol, 78 % yield) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 18H), 3.89 (s, 4H), 4.22 (s, 3H) 6.53- 6.62 (m, 3H), 7.41- 7.43 (m, 4H), 7.95- 7.97 (m, 4H).

1,2-bis((2-(4-tert-Butylphenyl)-1,3-dithian-2-yl)methyl)benzene (16). In a 50 mL round-bottomed flask 2-(4-tert-butylphenyl)-1,3-dithiane (1.0 g, 3.96 mmol) was added to THF (13 mL) to give a colorless solutionThe reaction was cooled to -78 °C and n-butyllithium 2.5 M in hexanes (1.98 mL, 4.95 mmol) was added dropwise to give an orange The reaction was kept at -78 °C for 30 minutes then warmed to room temp for 30 minutes. The reaction was then cooled back to -78 °C and 1,2-bis(bromomethyl)benzene (0.5 g, 1.9 mmol) in 20 mL of dry THF was added dropwise over 2 minutes. The reaction was allowed to warm to room temp over 30 minutes and stirred at room temp for 3.5 hours. The reaction was quenched with 30 mL water and separated. The aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20mL) then 20 mL brine then dried over $CaCl_2$. The solvent was removed under reduced pressure to yield 1,2-bis((2-(4-tert-butylphenyl)-1,3-dithian-2-yl)methyl)benzene (0.67 g, 1.11 mmol, 56 % yield) crude. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.35 (s, 18H), 1.90-1.94 (m, 4H), 2.22 (s, 4H), 2.44-2.62 (m, 8H), 6.96-6.99 (AA'MM', 2H), 7.06-7.09 (AA'MM', 2H), 7.23-7.26 (m, 4H) 7.41- 7.44 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.15, 27.51, 31.50,34.43, 46.39, 60.19, 125.43, 125.97, 129.05, 132.54, 134.37, 137.37, 150.24.

2,2'-(4,5-bis(Dodecyloxy)-1,2-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (16a). In a 50 mLround-bottomed flask2-phenyl-1,3-dithiane (0.5 g, 2.55 mmol) was

added to THF (25 mL) to give a colorless The reaction was cooled to -78 °C and n-butyllithium 2.5 M in hexanes (1.22 mL, 3.06 mmol) was added dropwise to give an orange The reaction was kept at -78 °C for 30 minutes then warmed to room temp for 30 minutes. The reaction was then cooled back to -78 °C and 1,2-bis(bromomethyl)-4,5-bis(dodecyloxy)benzene (1.61 g, 2.55 mmol) in 2 mL of dry THF was added dropwise over 2 minutes. The reaction was allowed to warm to room temp over 30 minutes and stirred at room temp for 3.5 hours. The reaction was quenched with 30 mL water and the layers separated. The aqueous phase was extracted with DCM (3 x 20 mL). The combined organics were washed with water (2 x 20mL) then 20mL brine then dried over $CaCl_2$. The solvent was removed under reduced pressure to yield 2,2'-(4,5-bis(dodecyloxy)-1,2-phenylene)bis(methylene)bis(2-phenyl-1,3-dithiane) (0.98 g, 1.13 mmol, 14 % yield) crude. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, 6H), 1.20-1.30 (m, 26), 1.35 (s, 18H), 1.63- 1.71 (m, 4H), 1.83-1.90 (m, 4H), 2.51-2.59 (m, 8H), 2.70 (s, 4H), 3.61 (t, 4H), 6.19 (s, 2H), 7.17-7.26 (m, 6H), 7.59- 7.61 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.15, 22.73, 25.10, 26.02, 27.59, 29.23, 29.41, 29.52, 29.69, 29.70, 29.75, 31.97, 46.42, 60.70, 68.49, 116.54, 126.26, 126.88, 128.36, 129.81, 140.61, 146.46.

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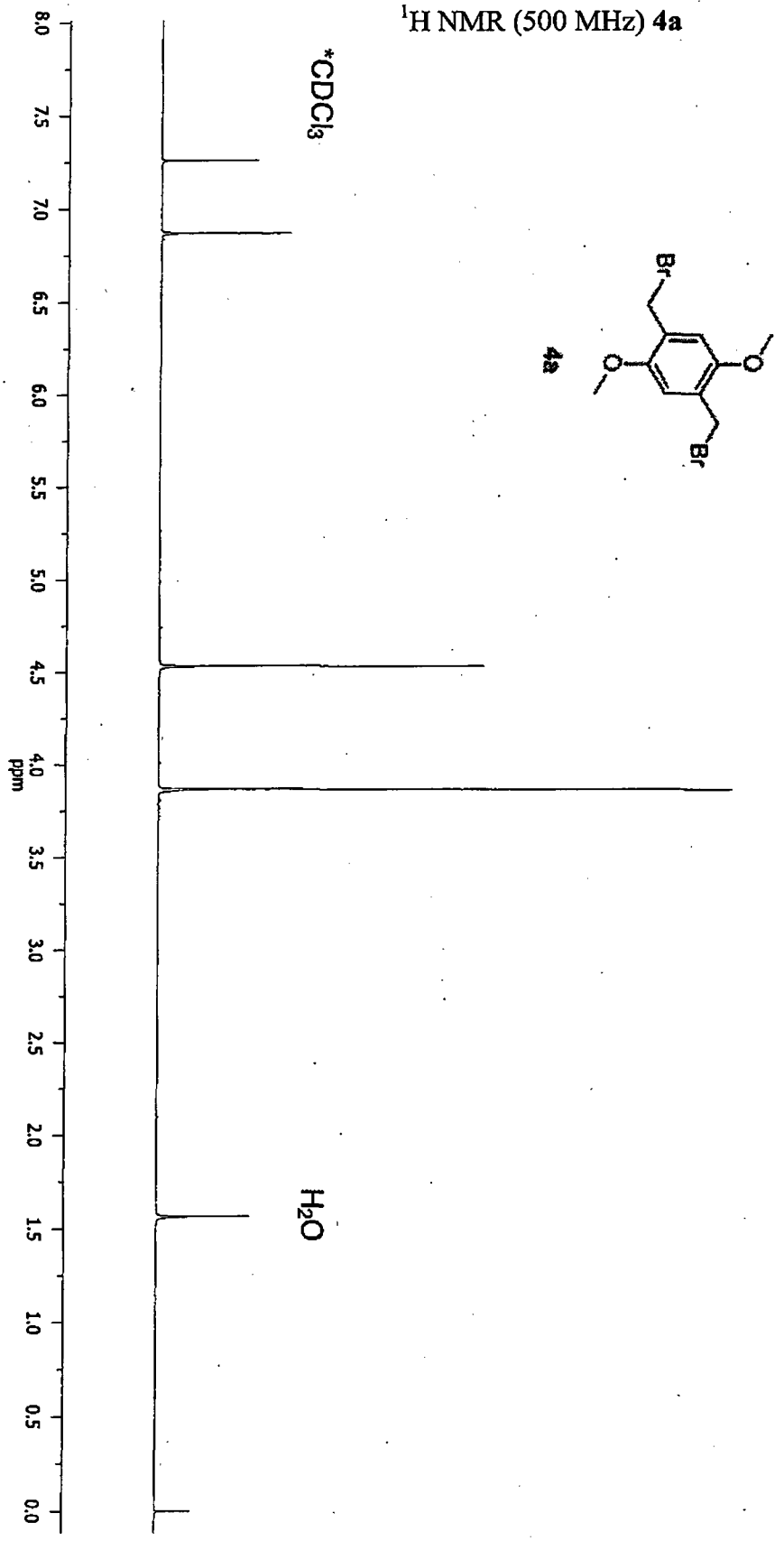
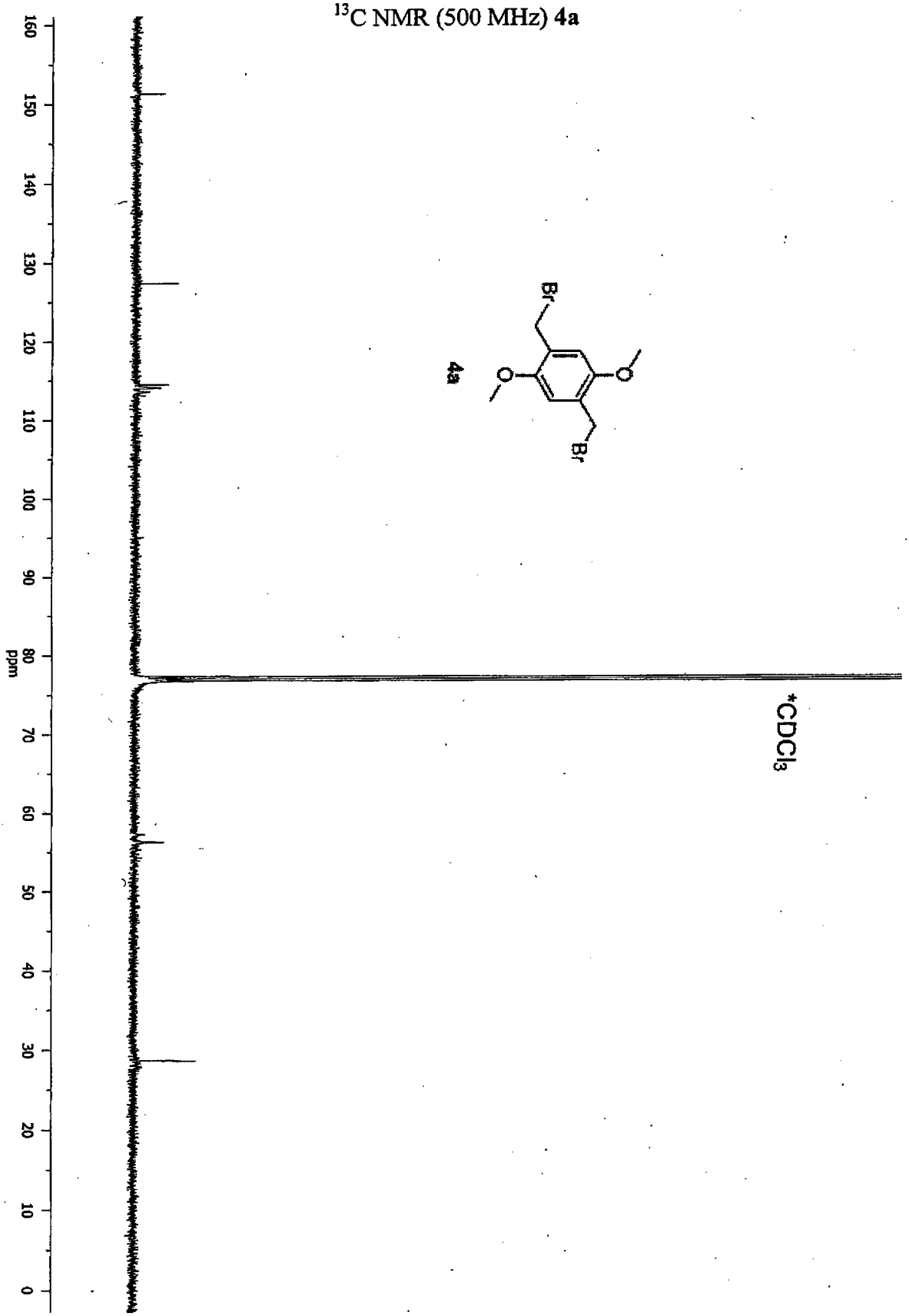
APPENDIX

^{1}H NMR (500 MHz) **4a**

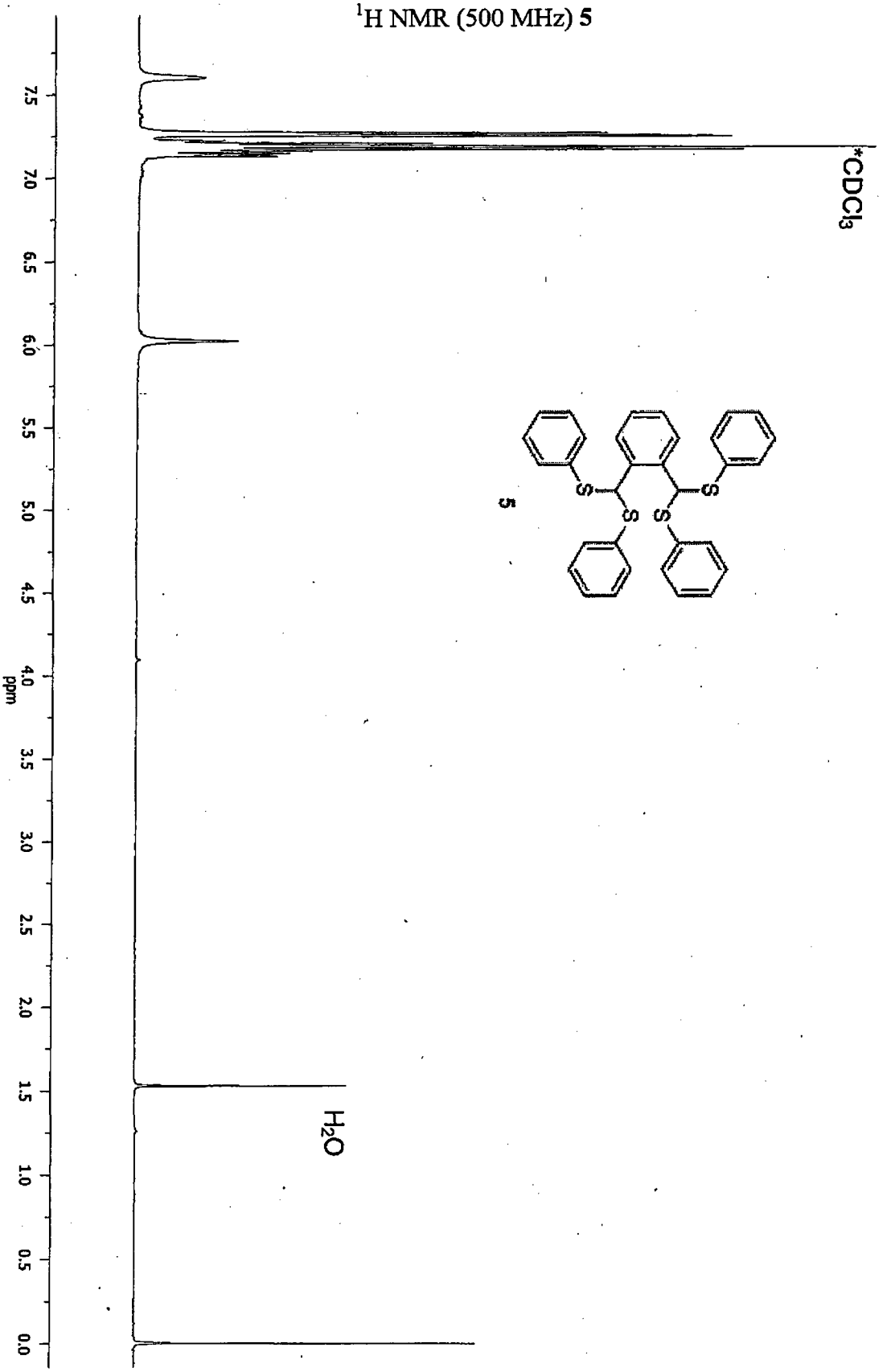


4a

^{13}C NMR (500 MHz) **4a**

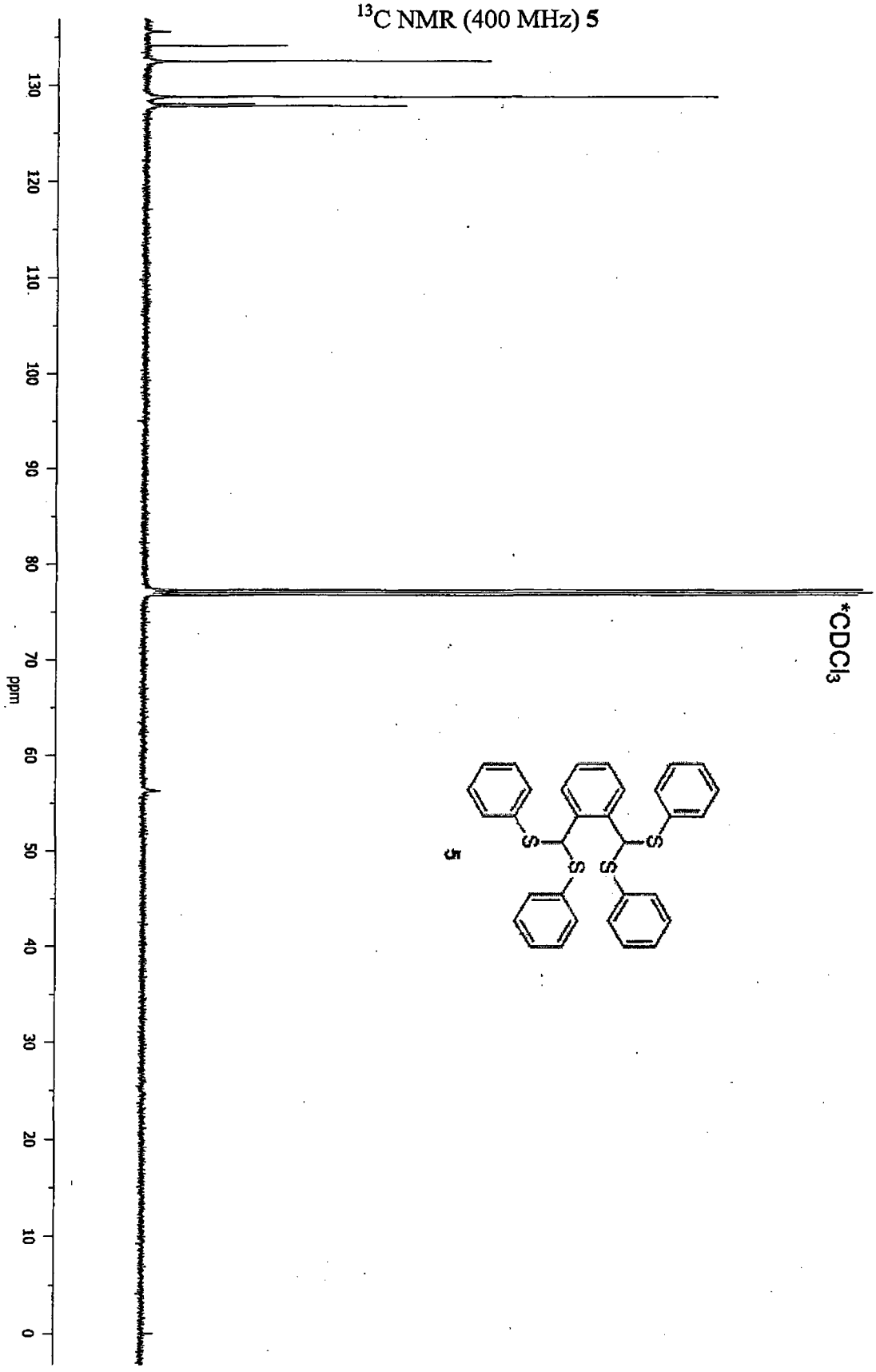


^{1}H NMR (500 MHz) **5**



5

^{13}C NMR (400 MHz) **5**



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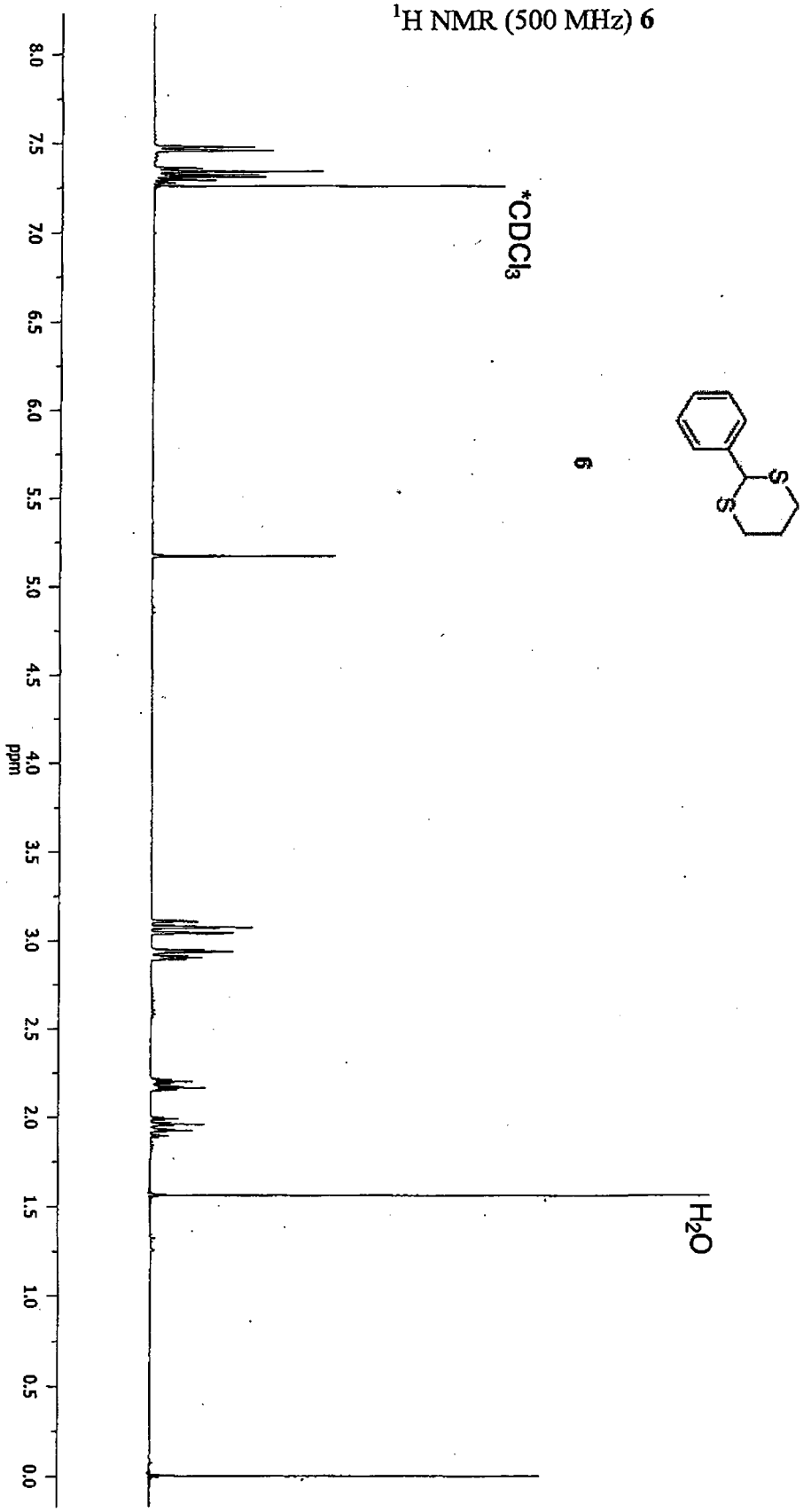
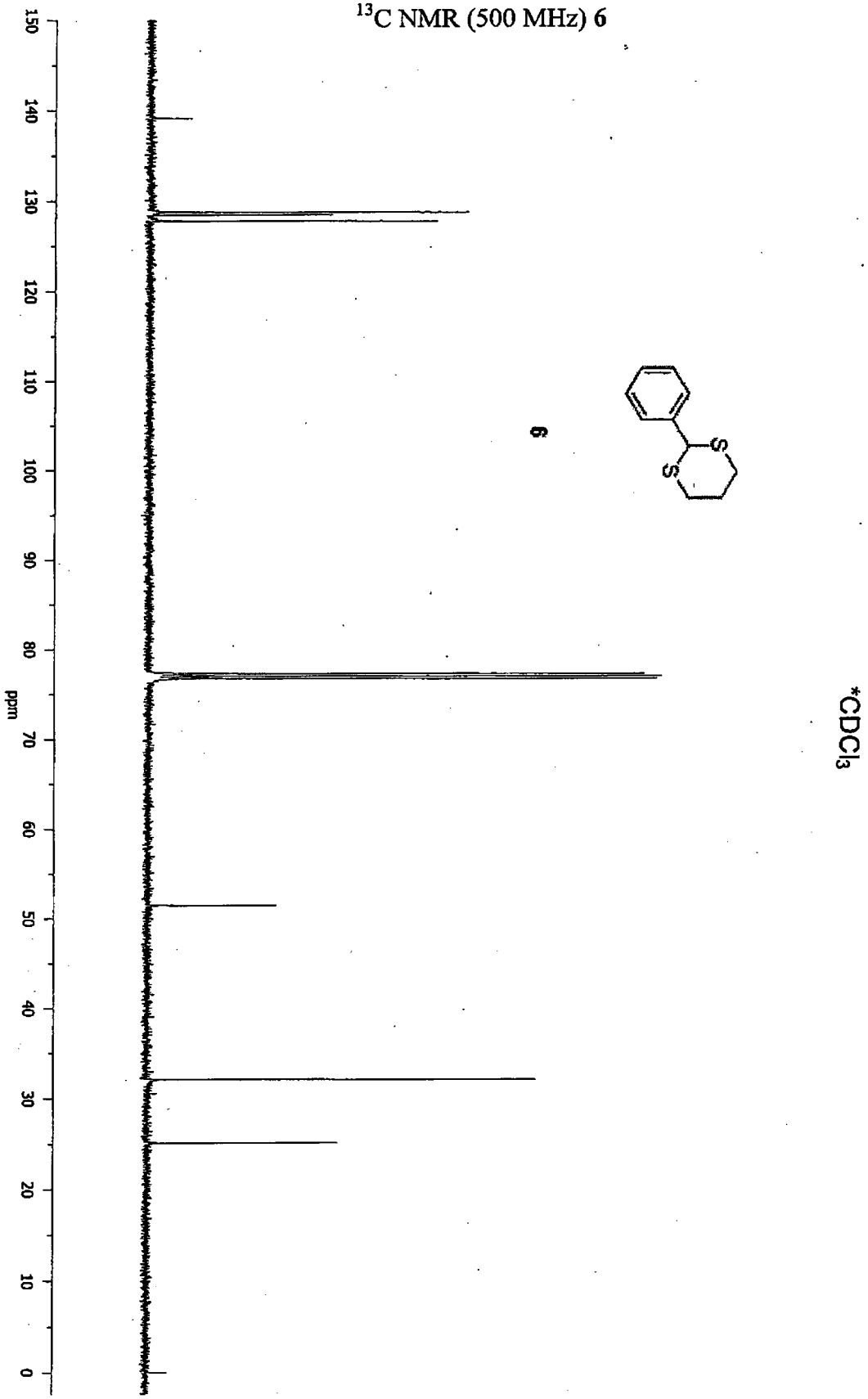
^{1}H NMR (500 MHz) **6**

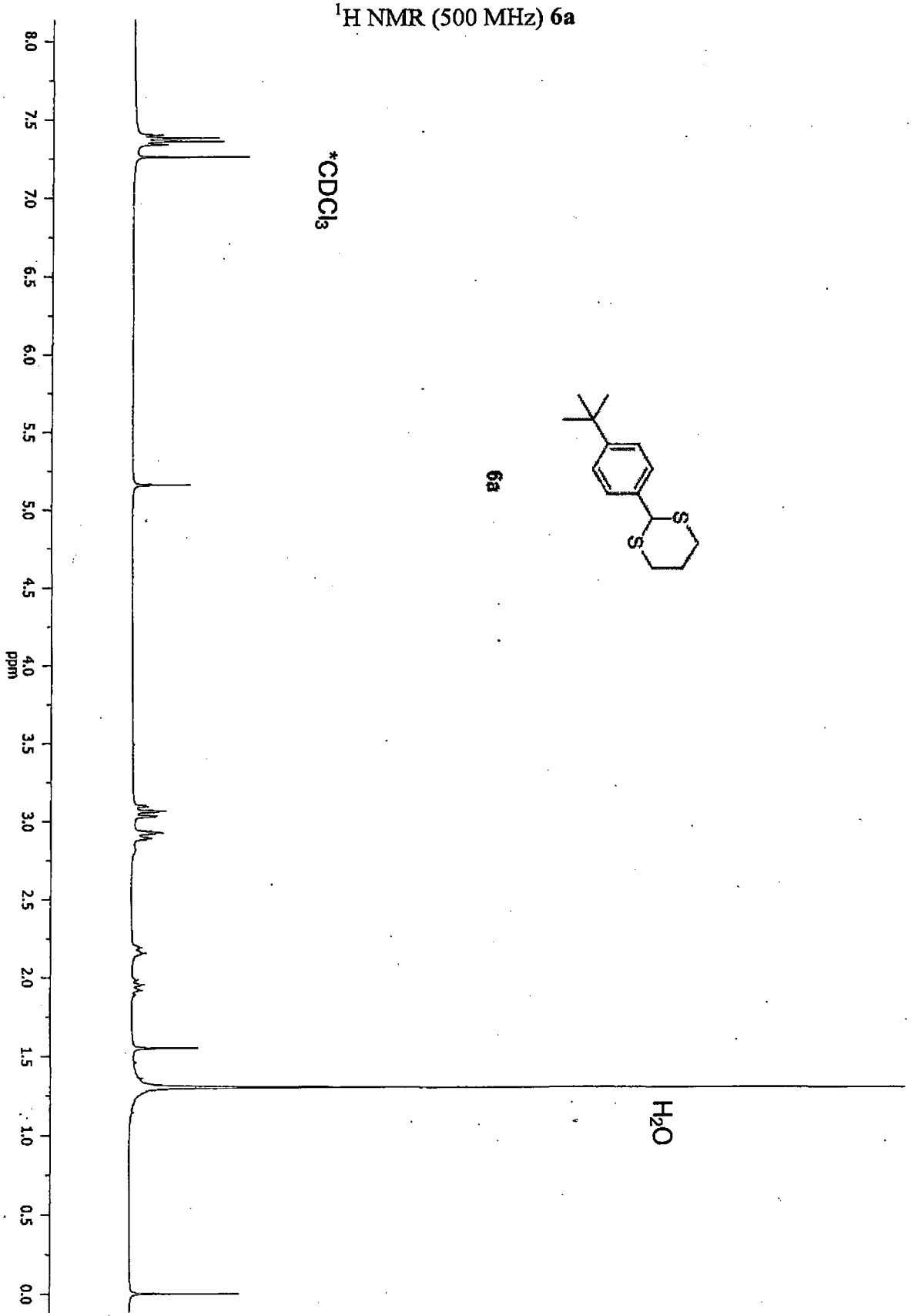


6

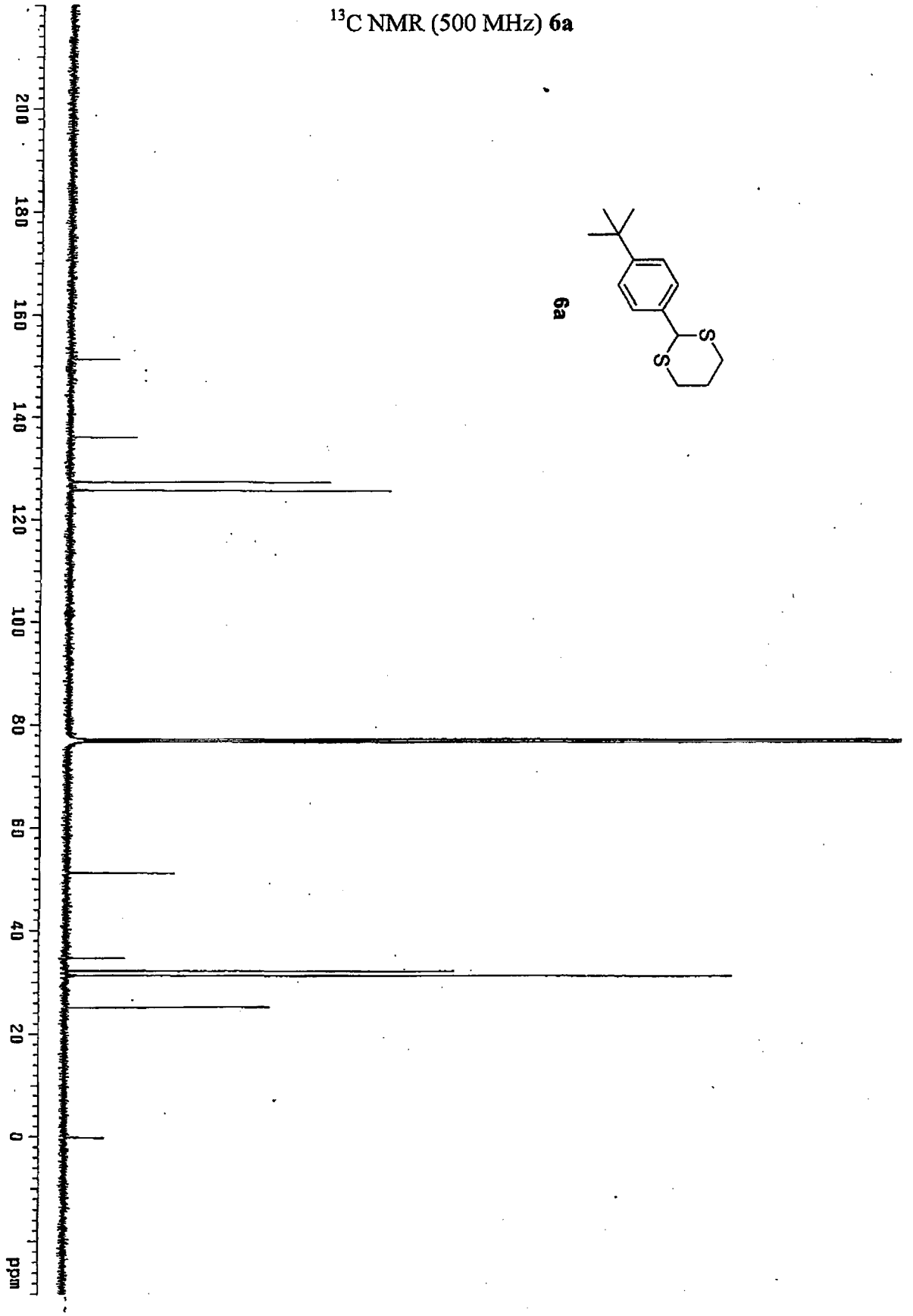
^{13}C NMR (500 MHz) **6**



^{1}H NMR (500 MHz) **6a**

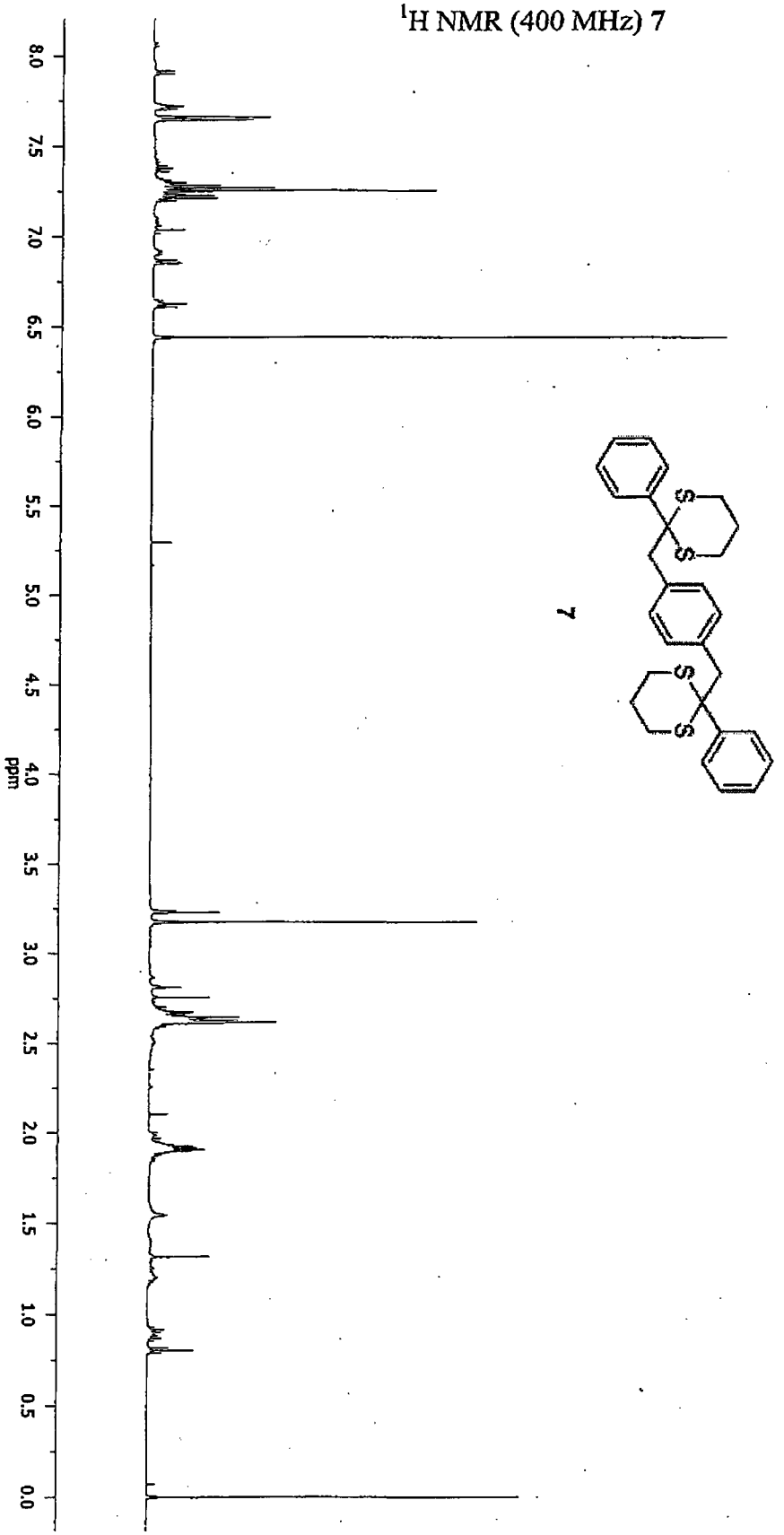


^{13}C NMR (500 MHz) **6a**



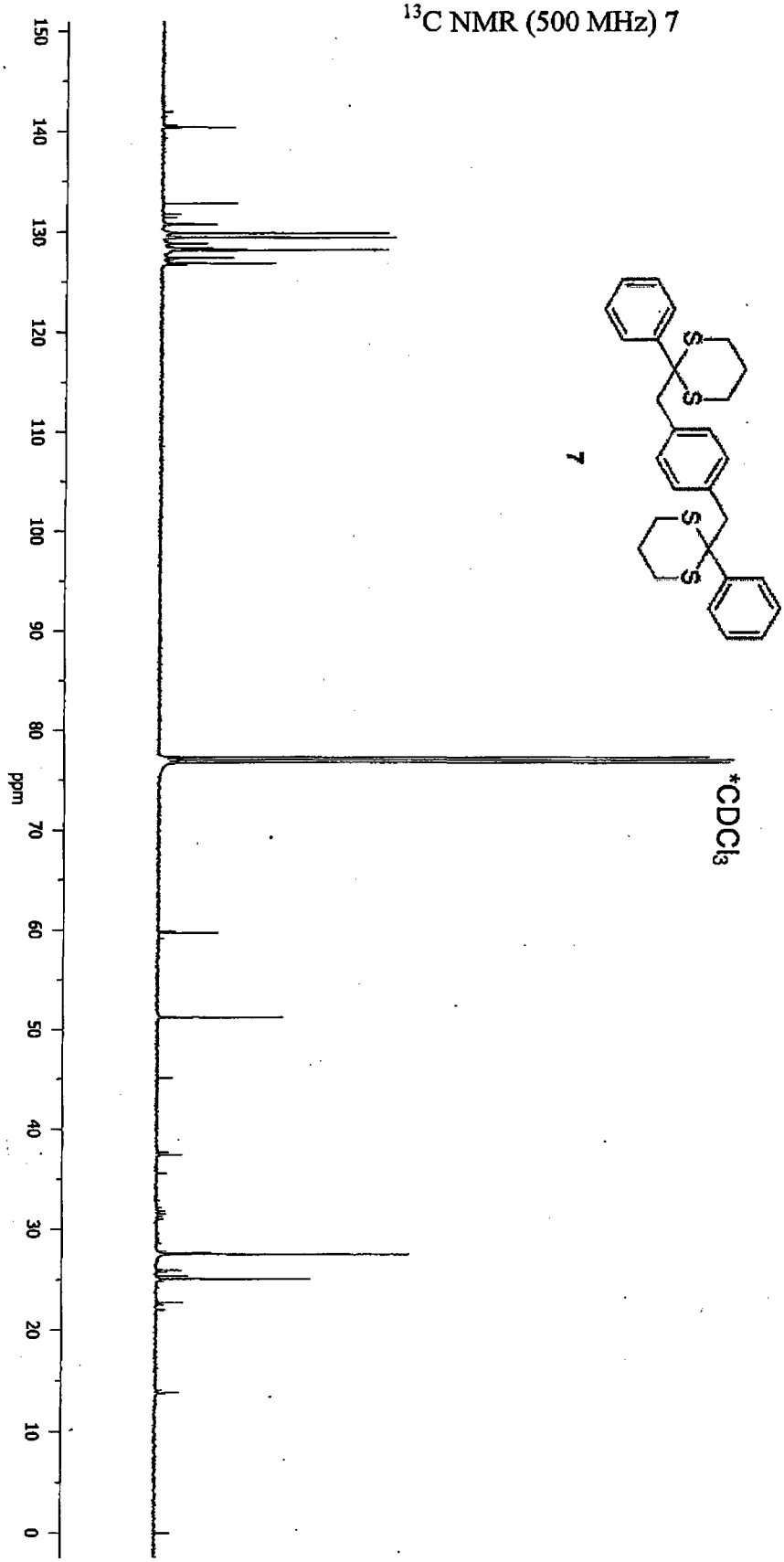
6a

^{1}H NMR (400 MHz) 7

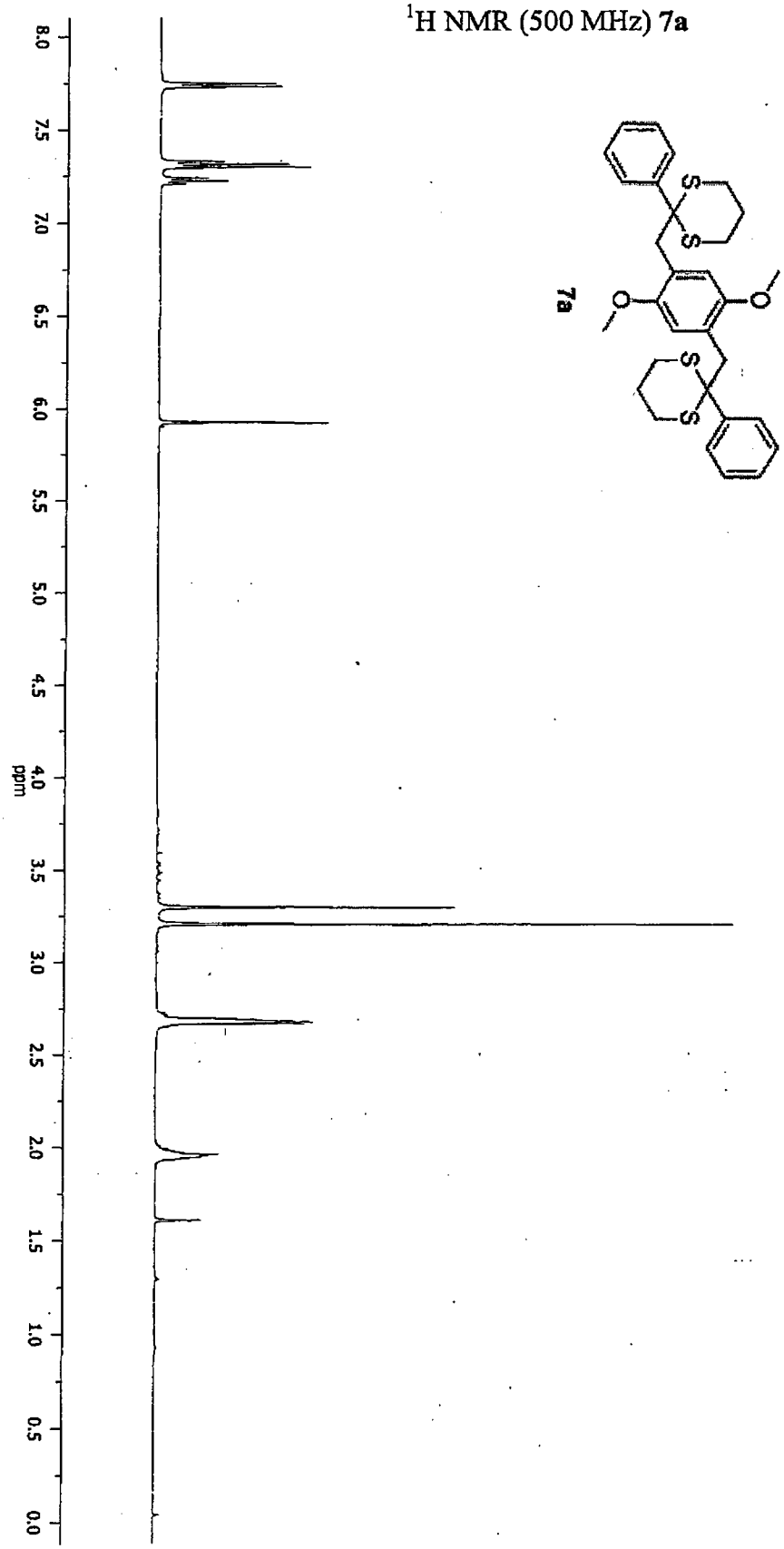


7

^{13}C NMR (500 MHz) 7

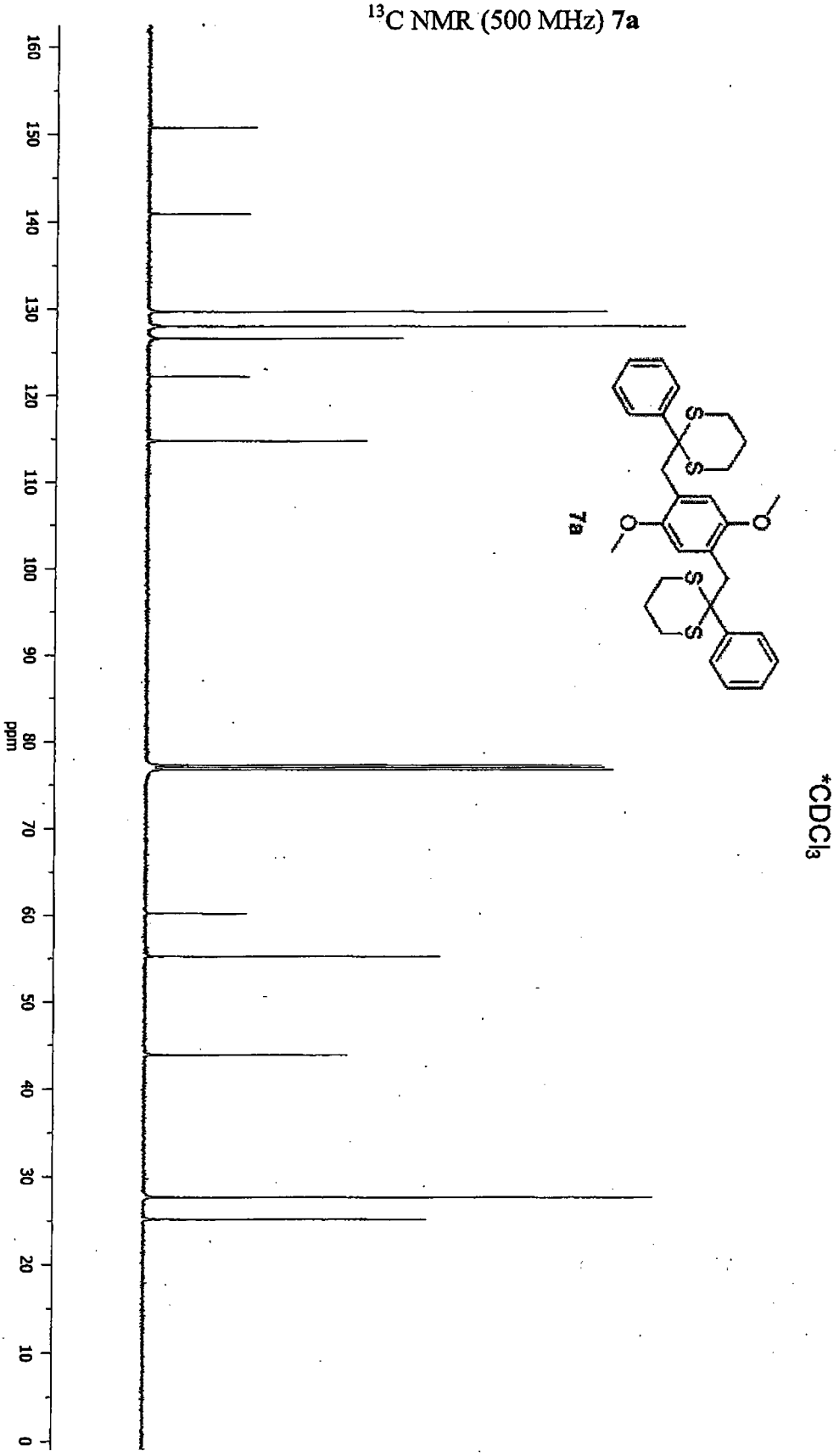


^{1}H NMR (500 MHz) **7a**

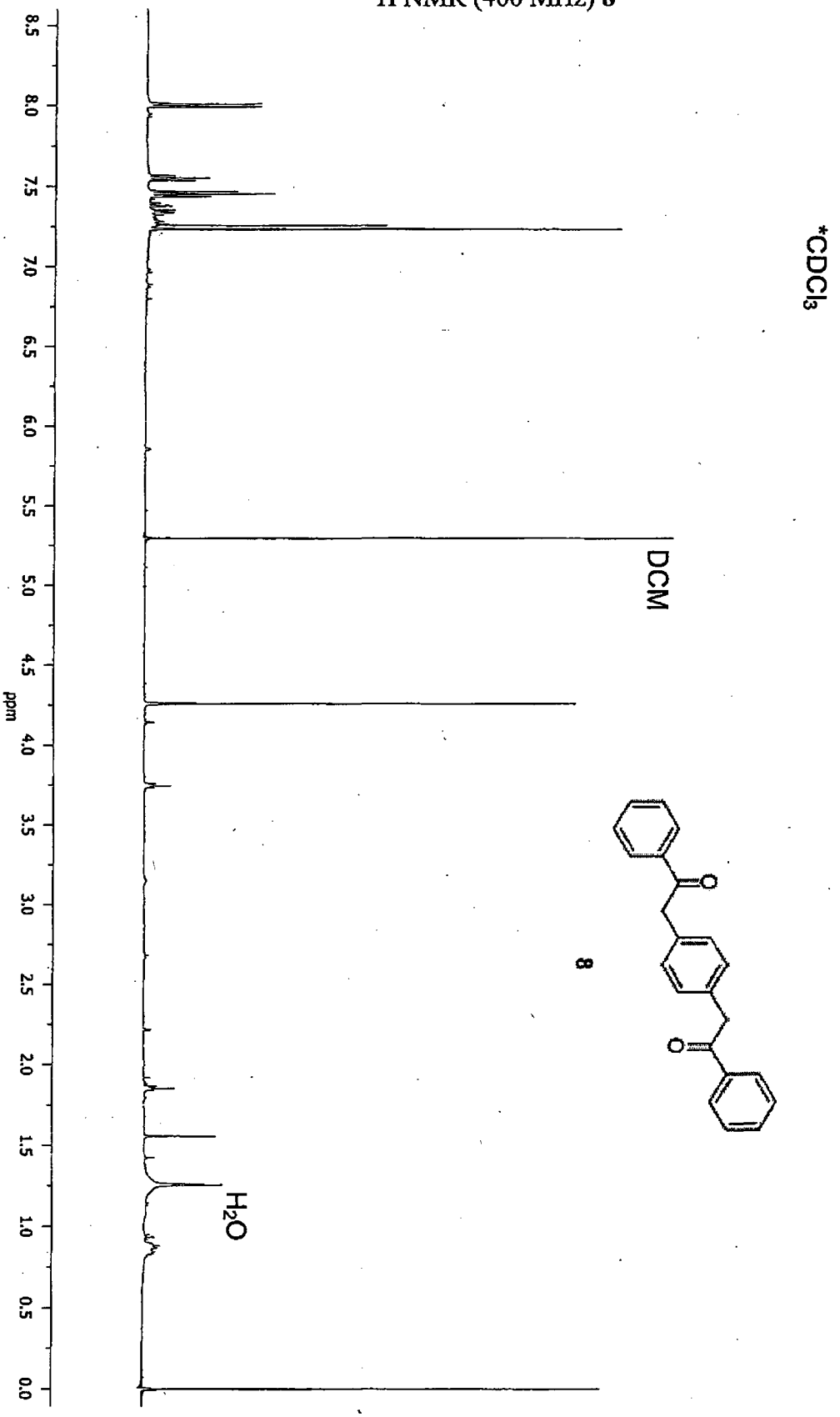


7a

^{13}C NMR (500 MHz) **7a**

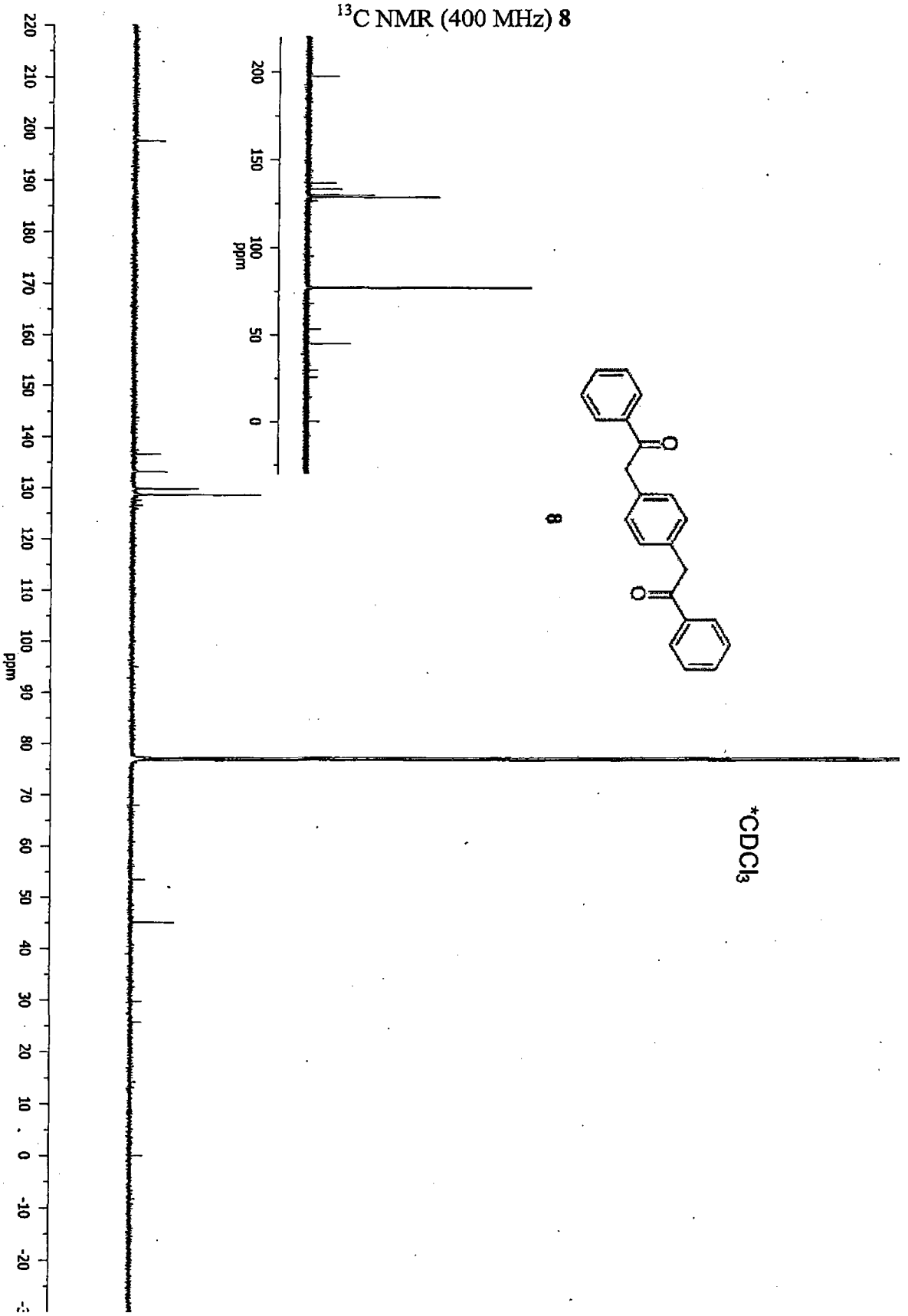


^{1}H NMR (400 MHz) **8**

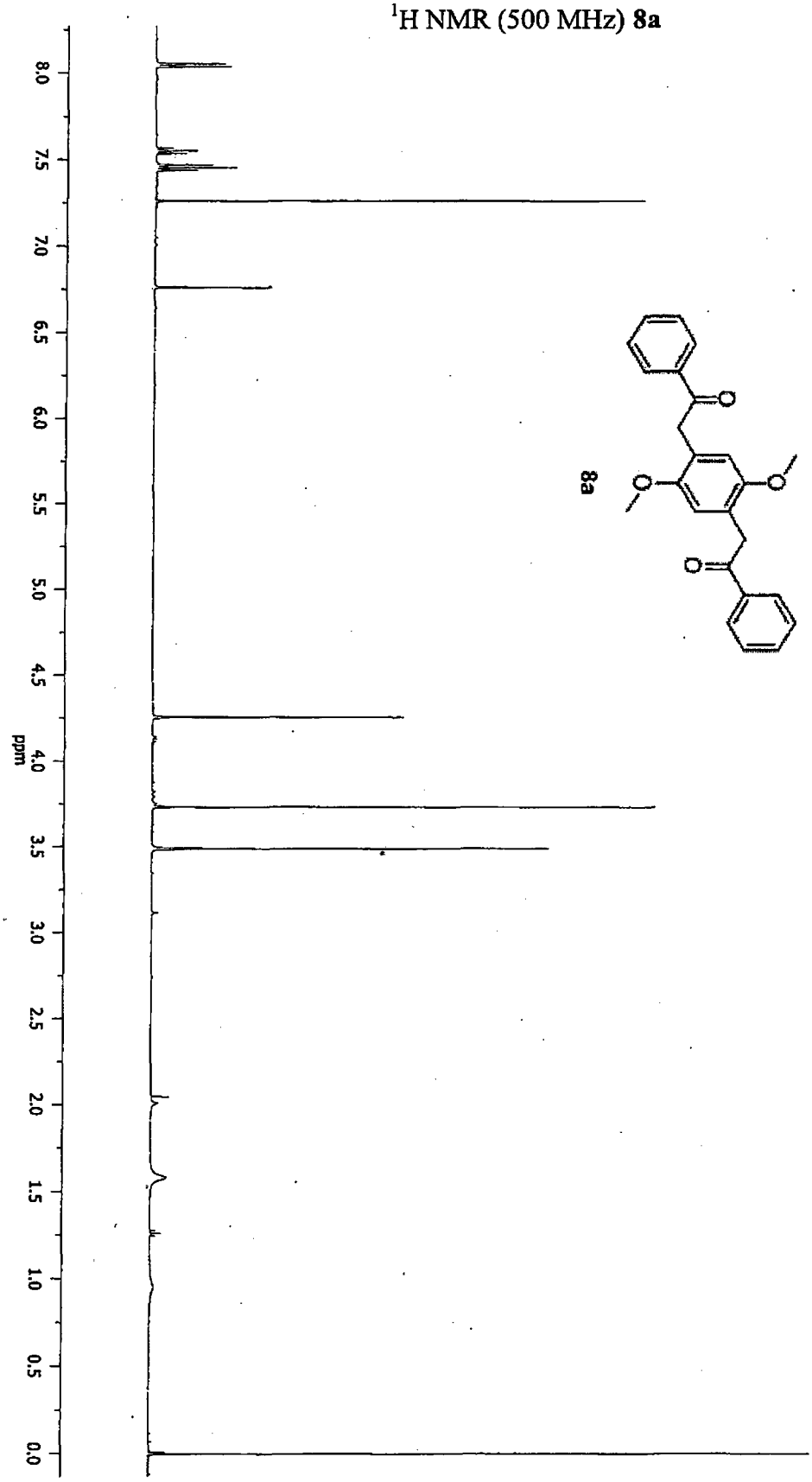


8

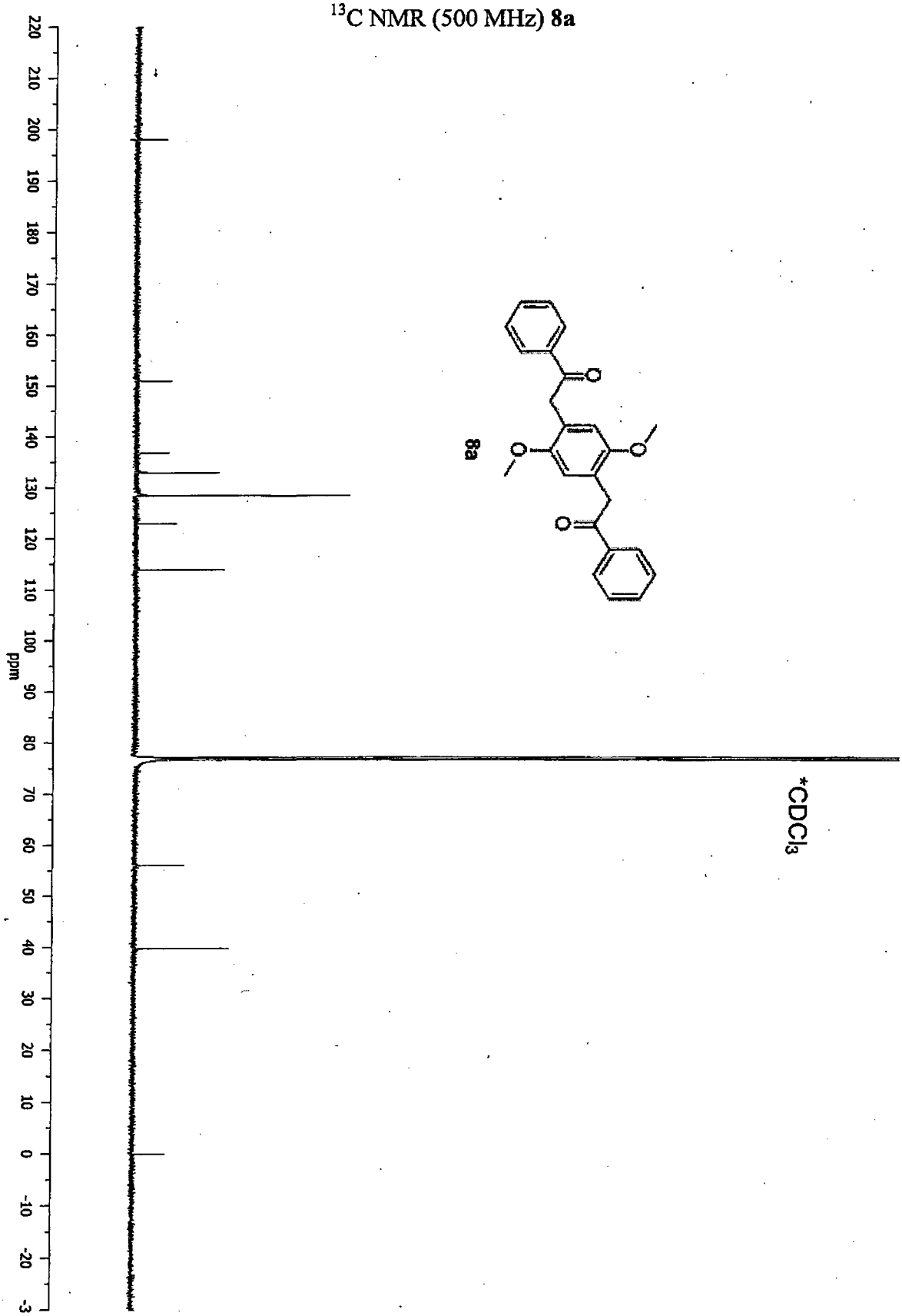
^{13}C NMR (400 MHz) **8**



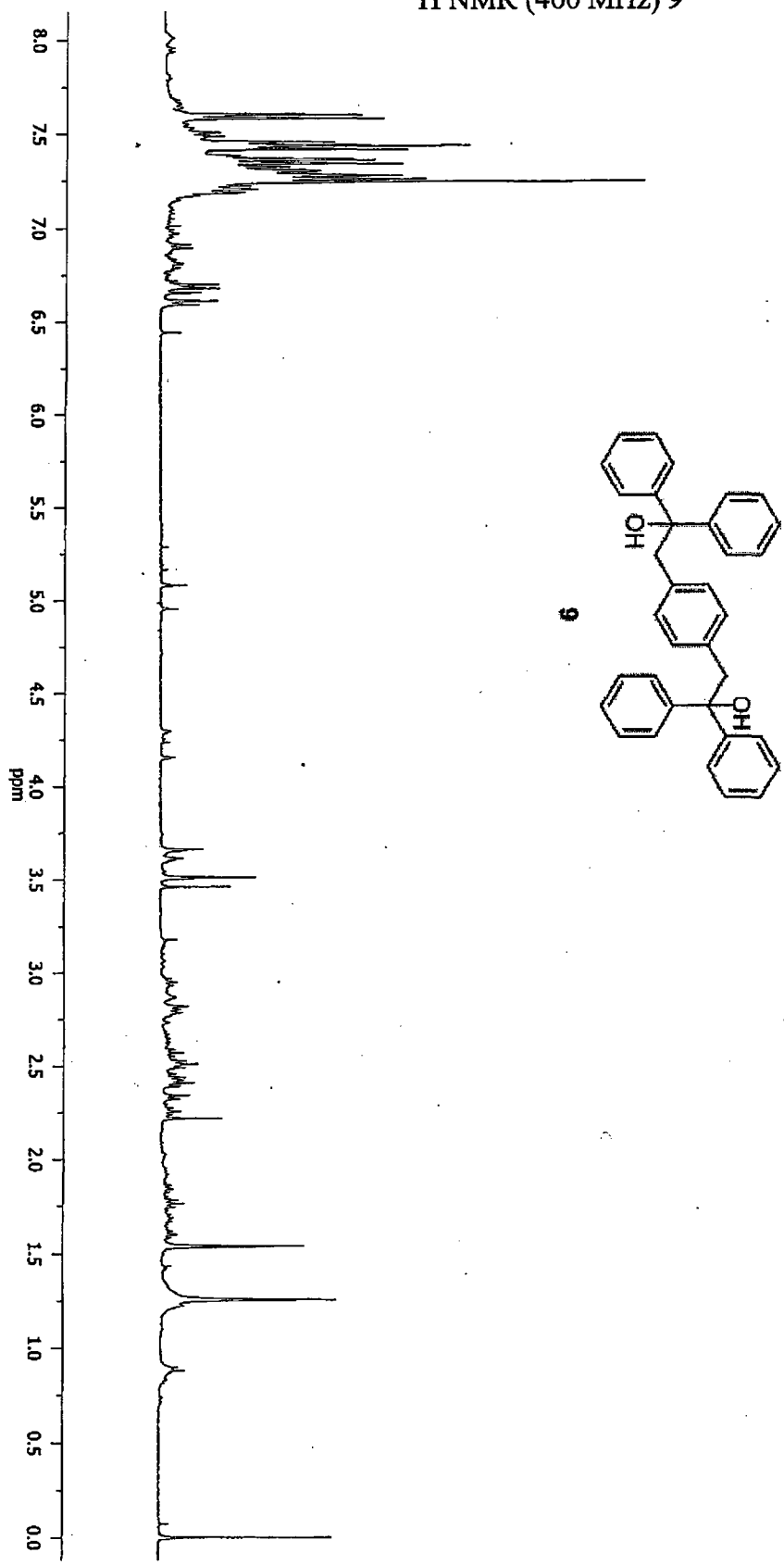
^{1}H NMR (500 MHz) **8a**



^{13}C NMR (500 MHz) **8a**

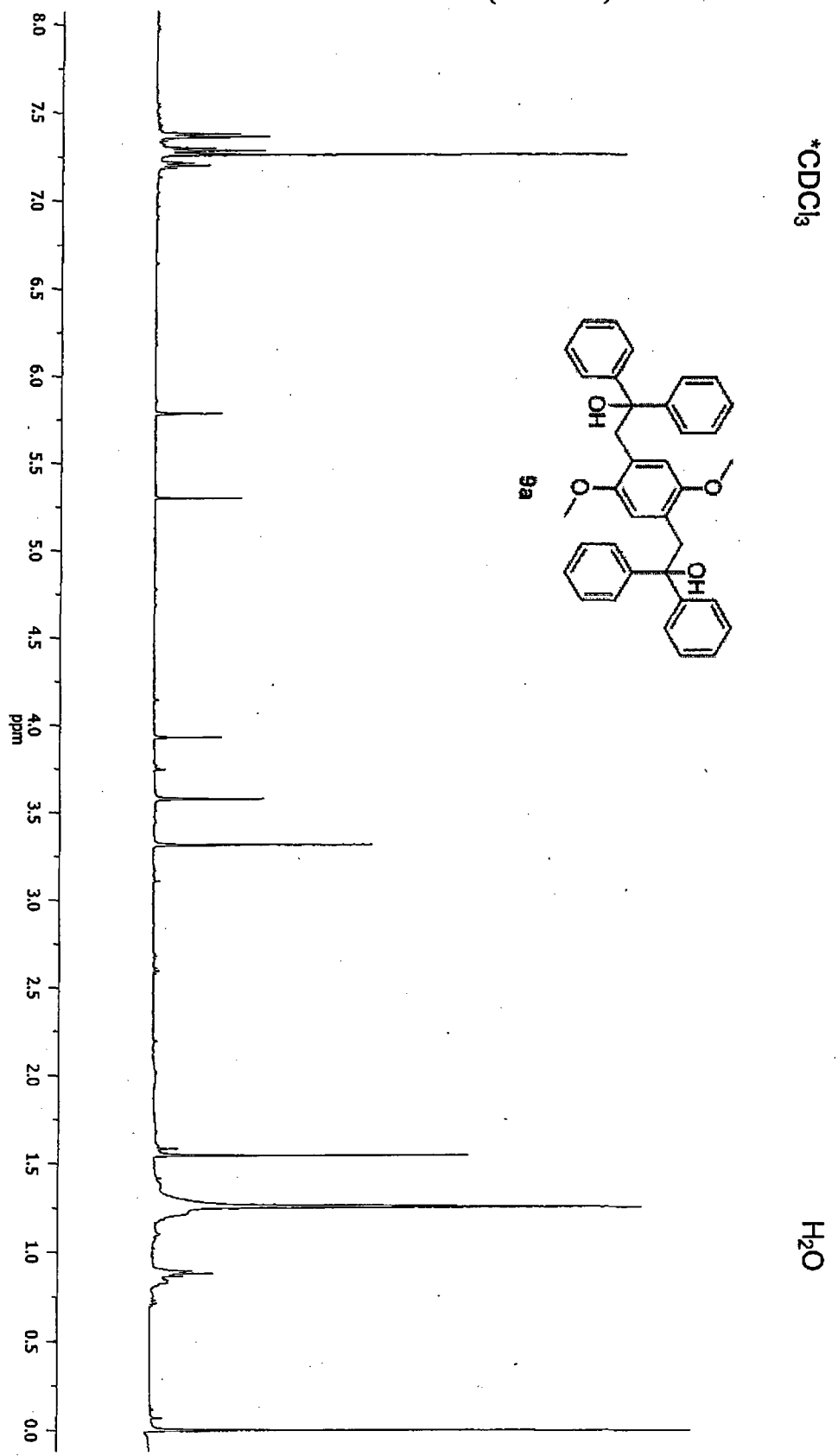


^{1}H NMR (400 MHz) **9**

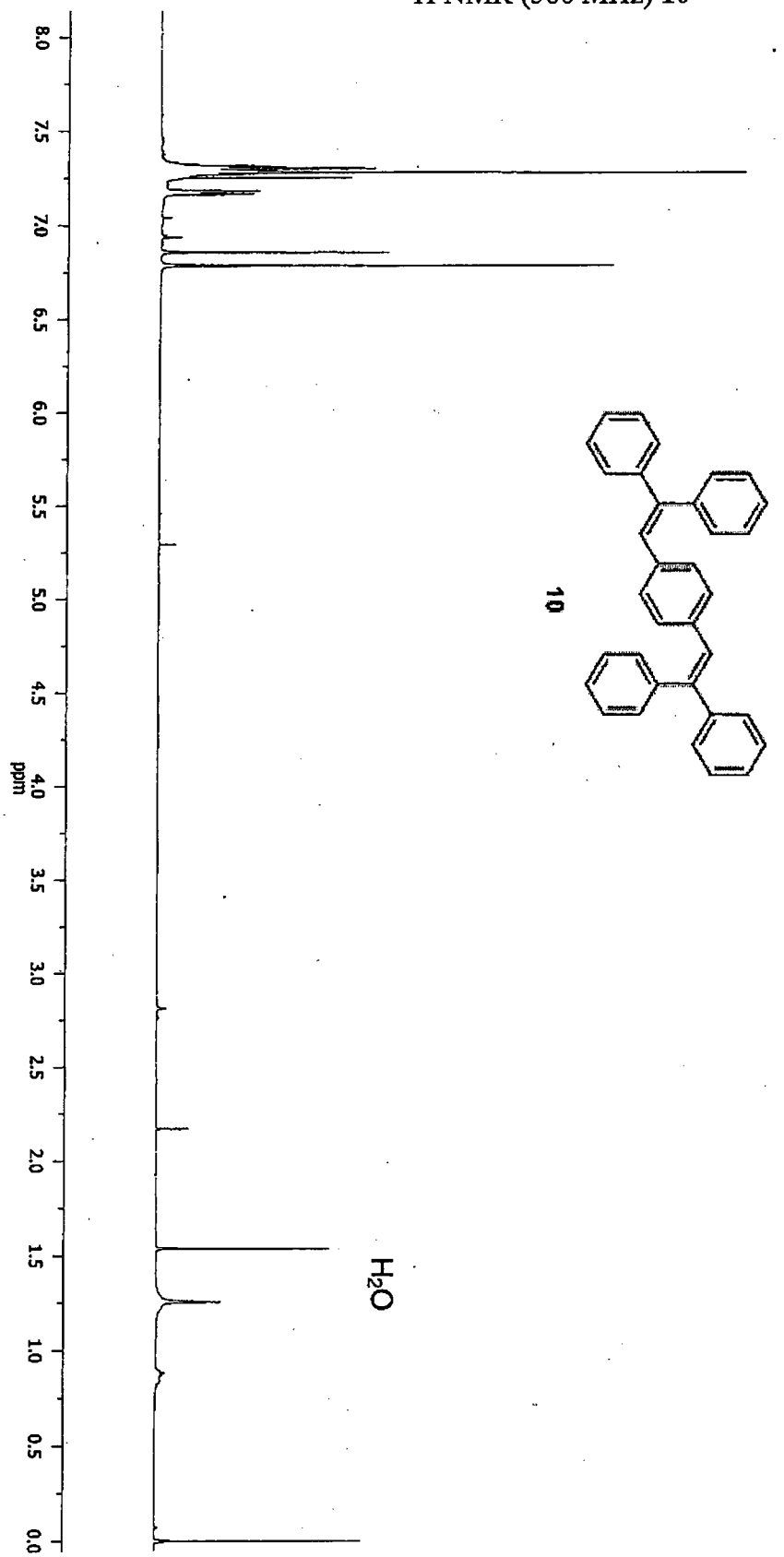


9

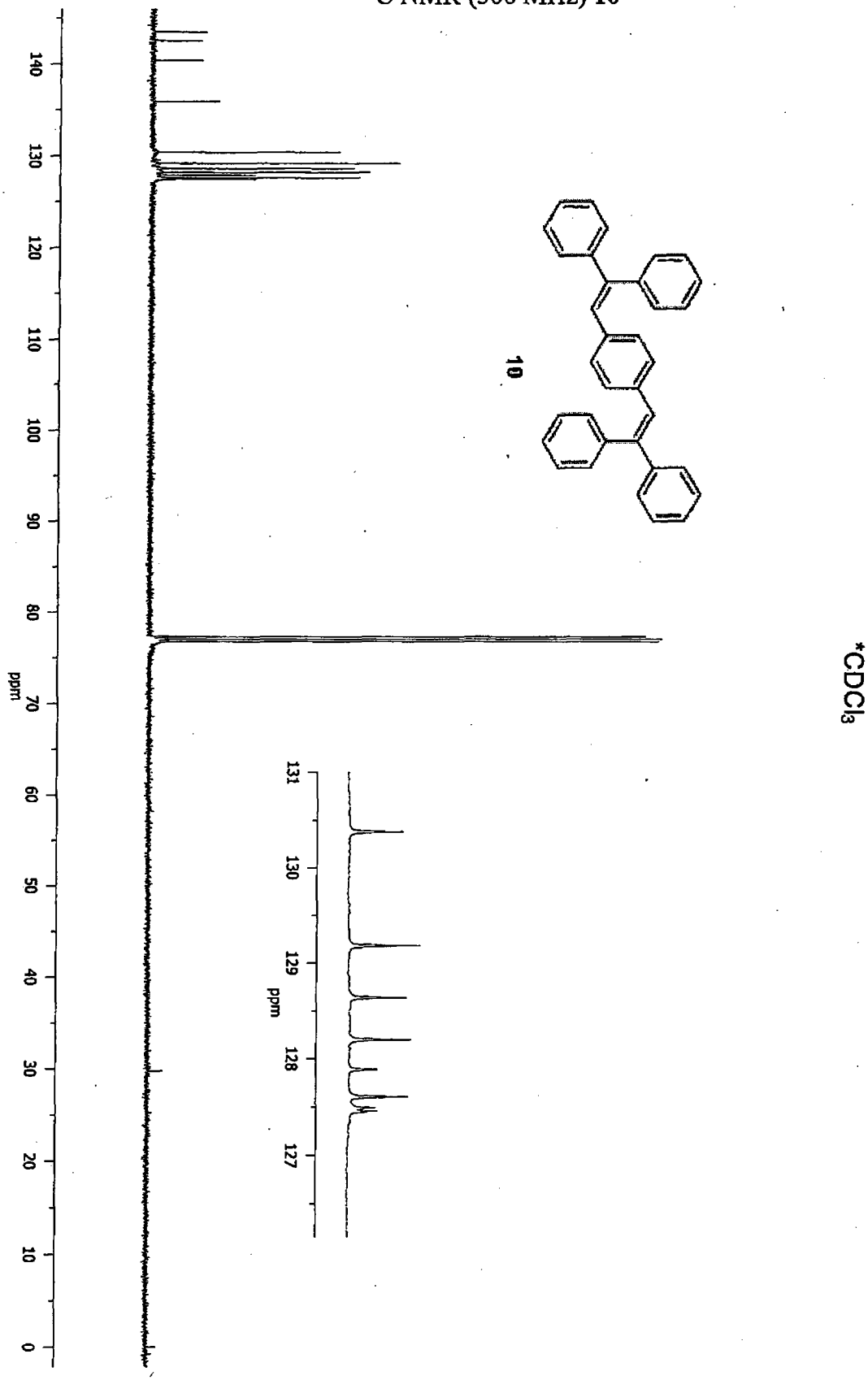
^{1}H NMR (400 MHz) **9a**



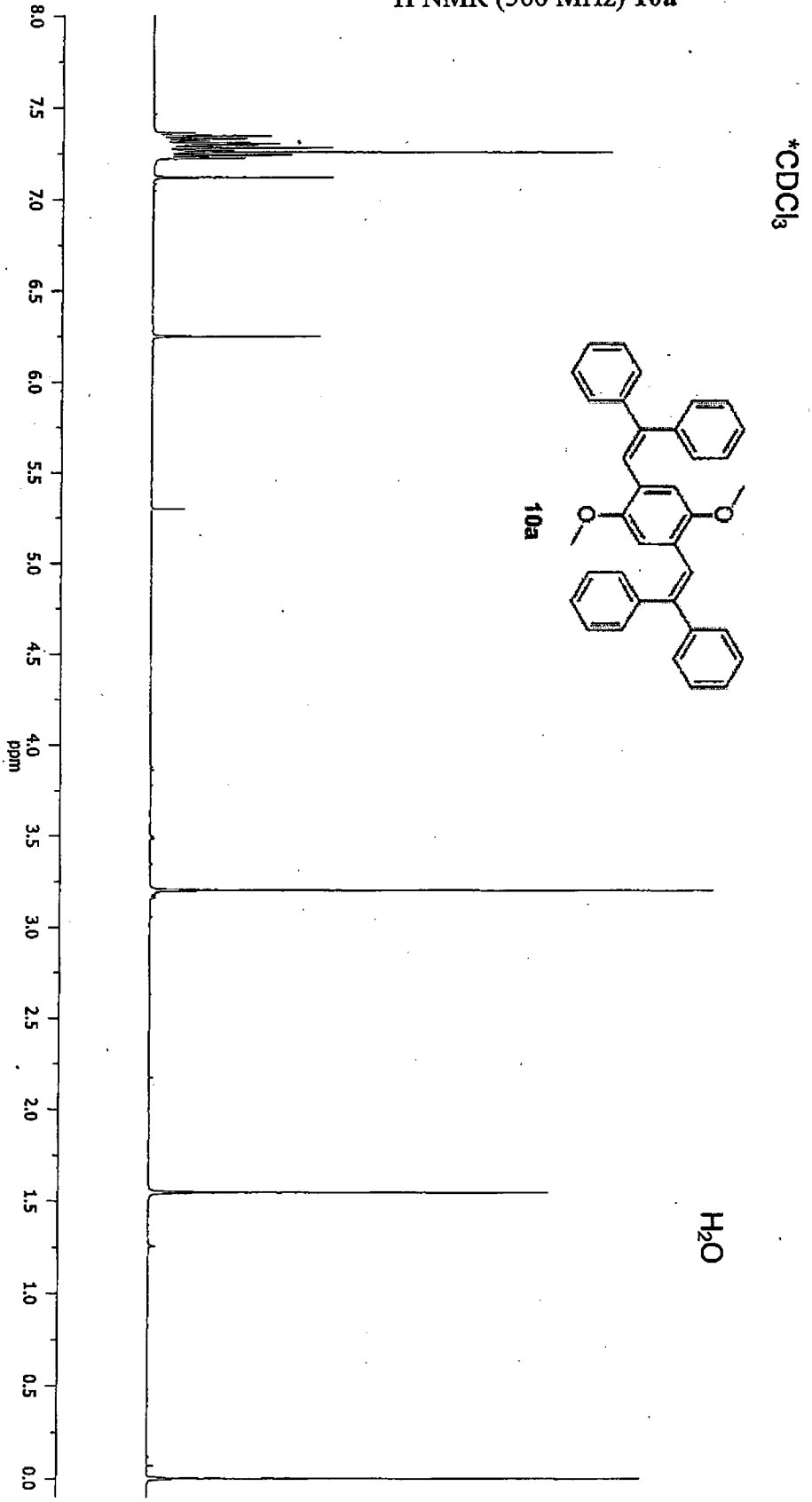
^{1}H NMR (500 MHz) **10**



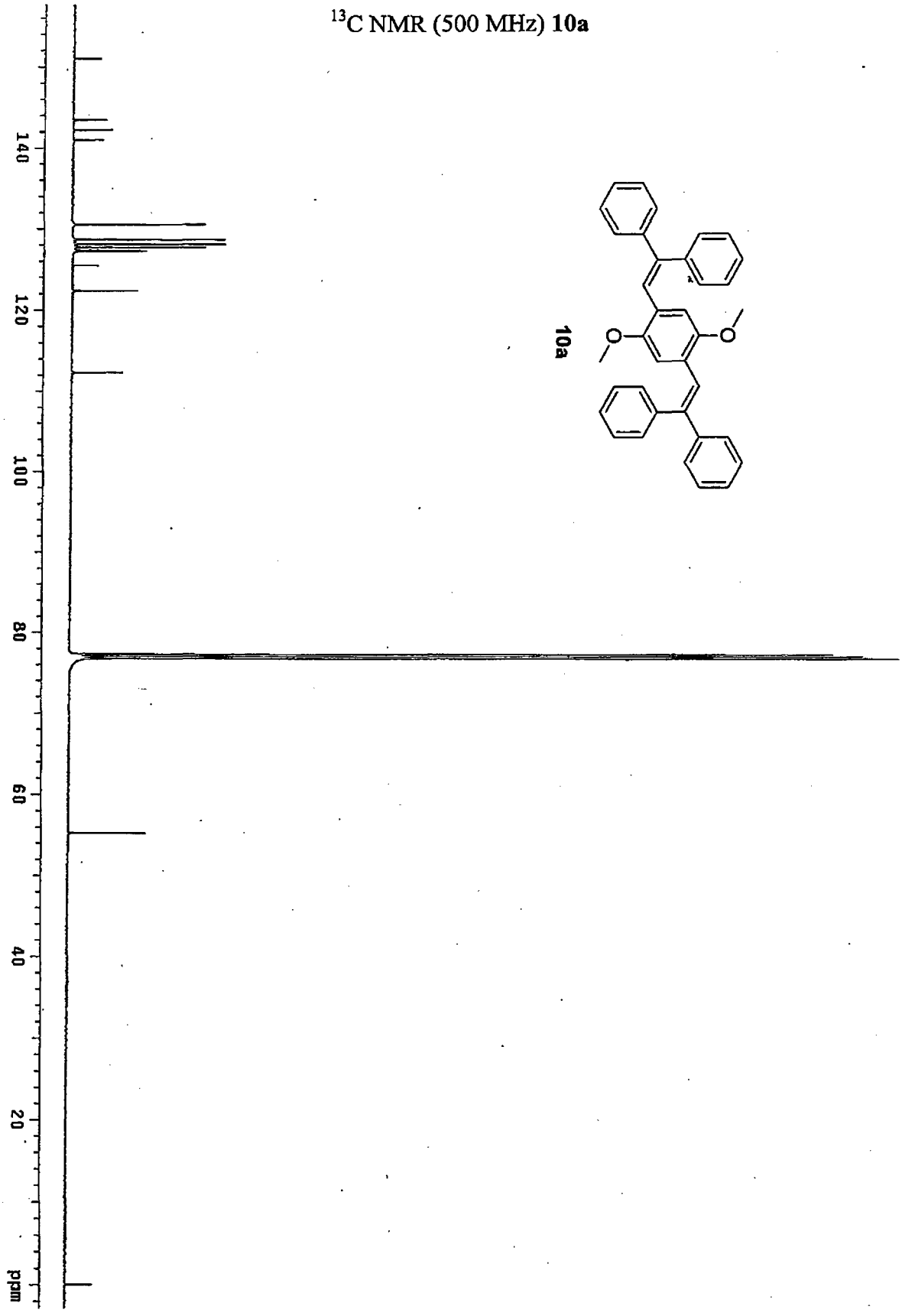
^{13}C NMR (500 MHz) **10**



^{1}H NMR (500 MHz) **10a**

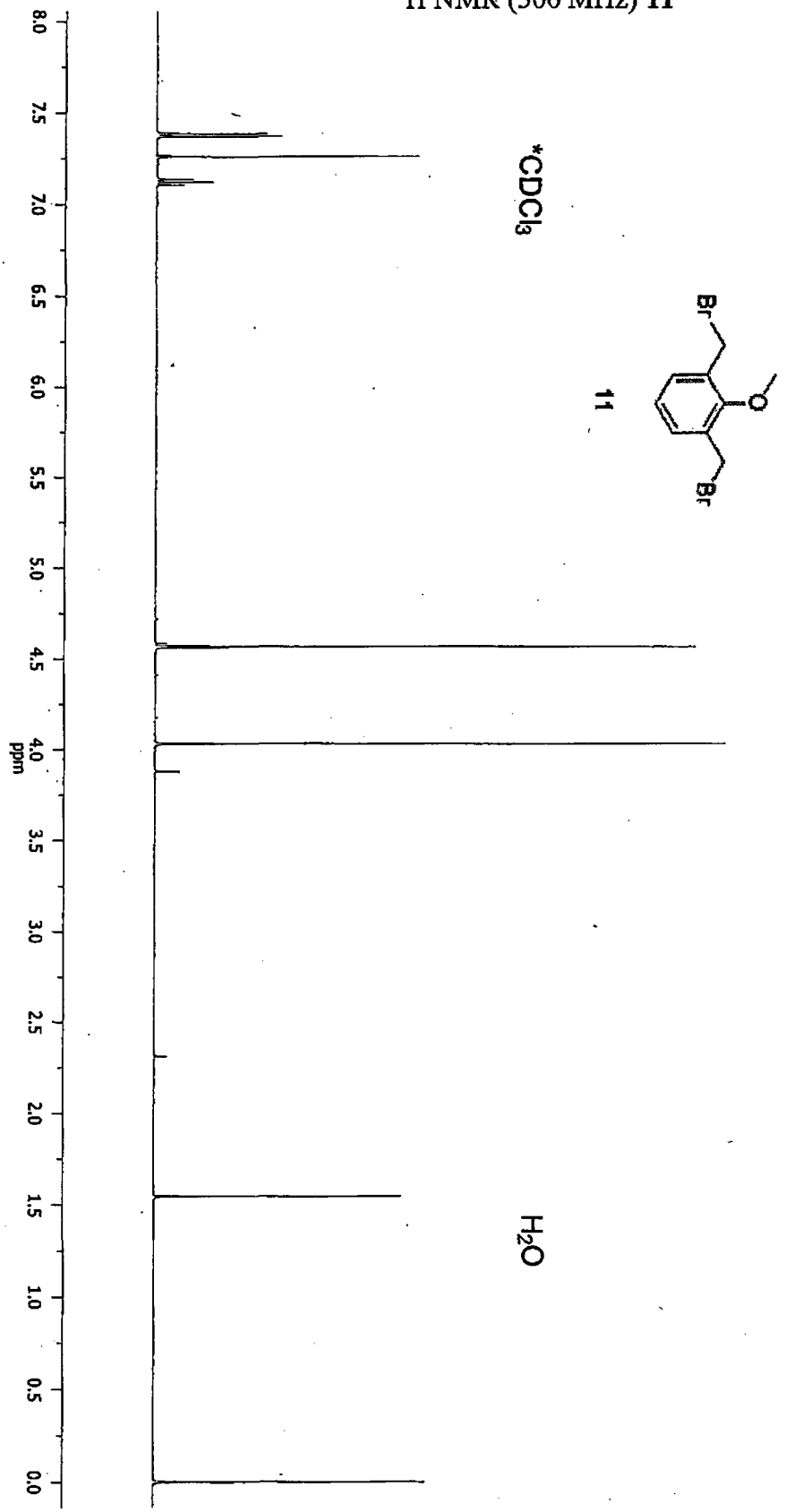


^{13}C NMR (500 MHz) **10a**



10a

^{1}H NMR (500 MHz) **11**



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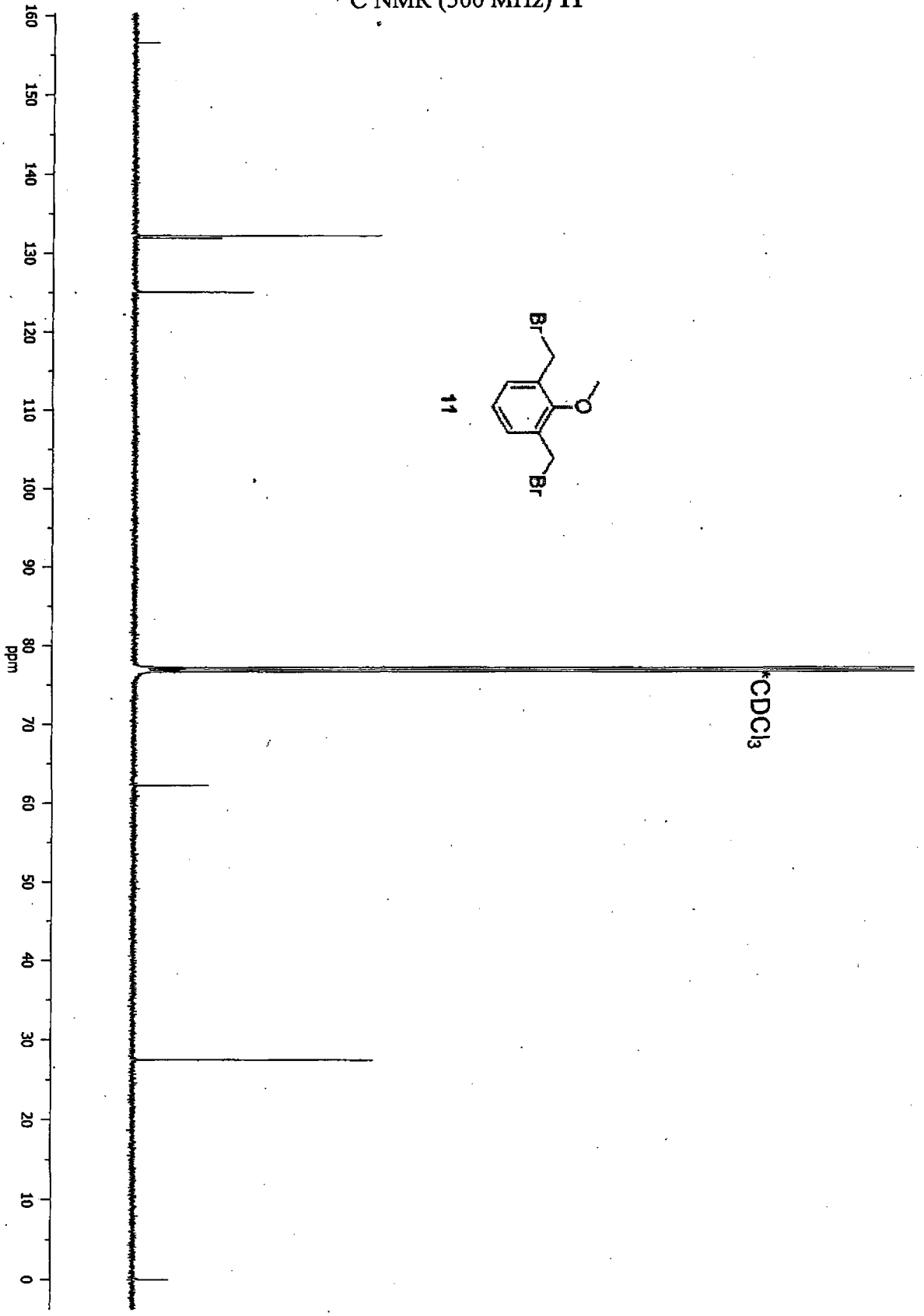
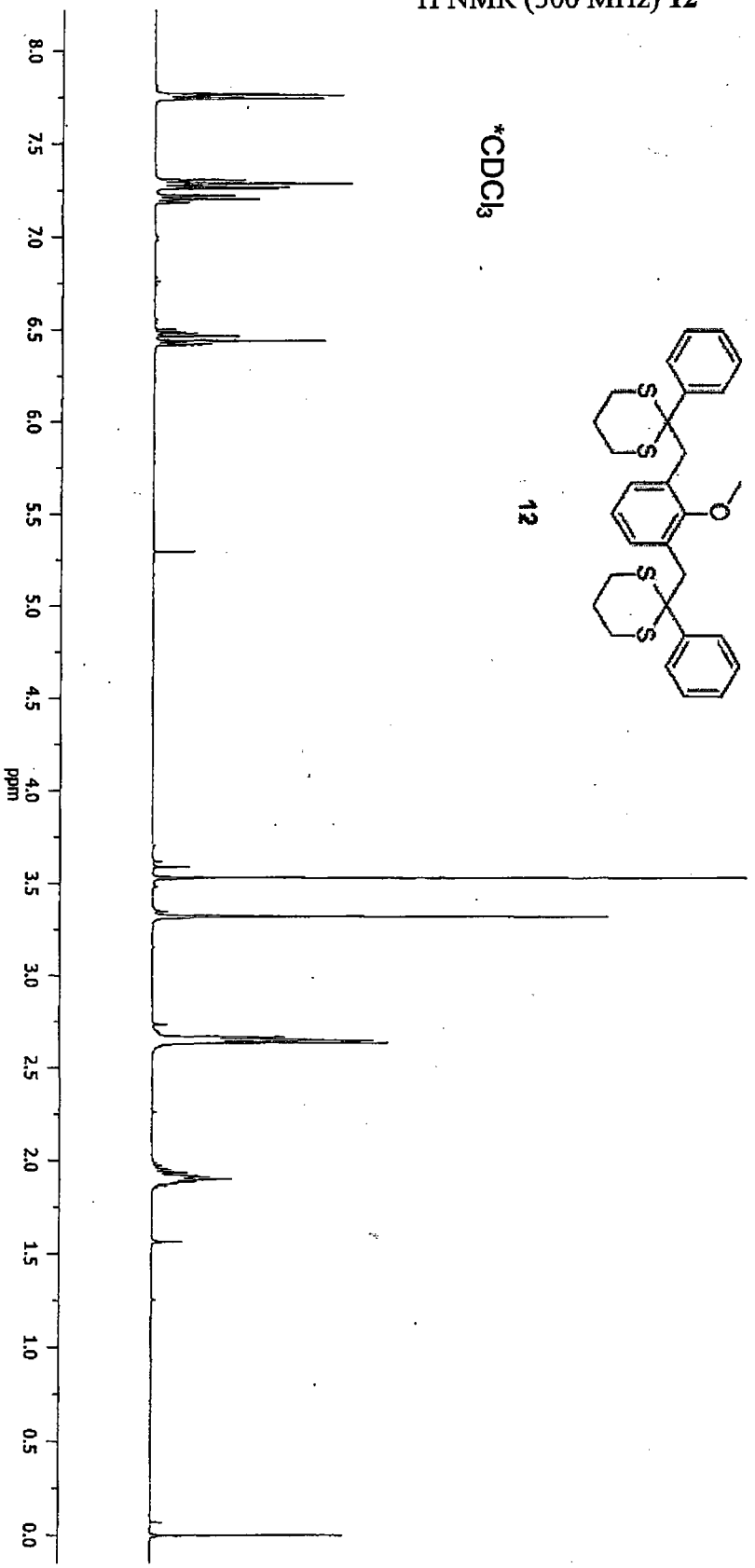


^{1}H NMR (500 MHz) **12**



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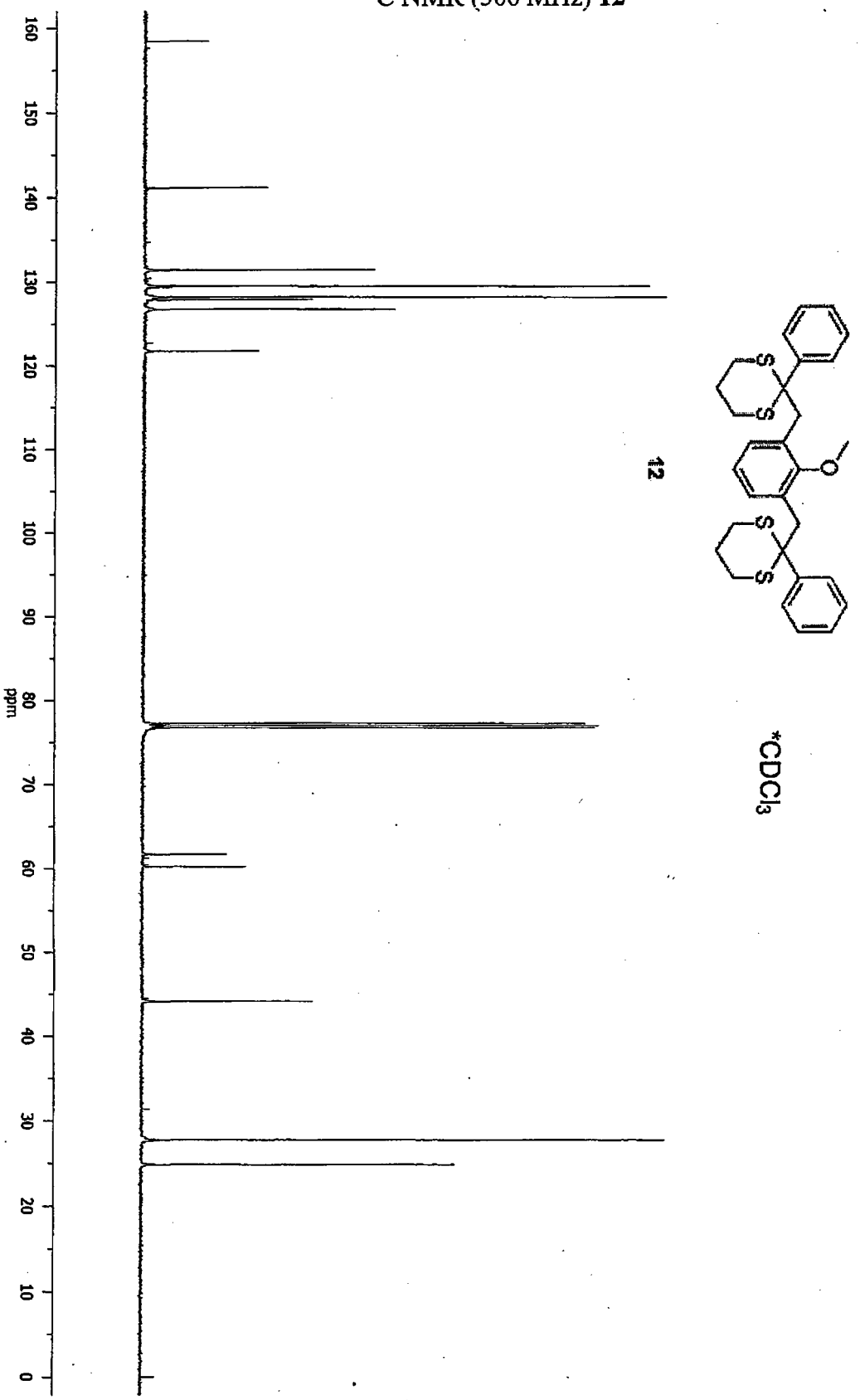

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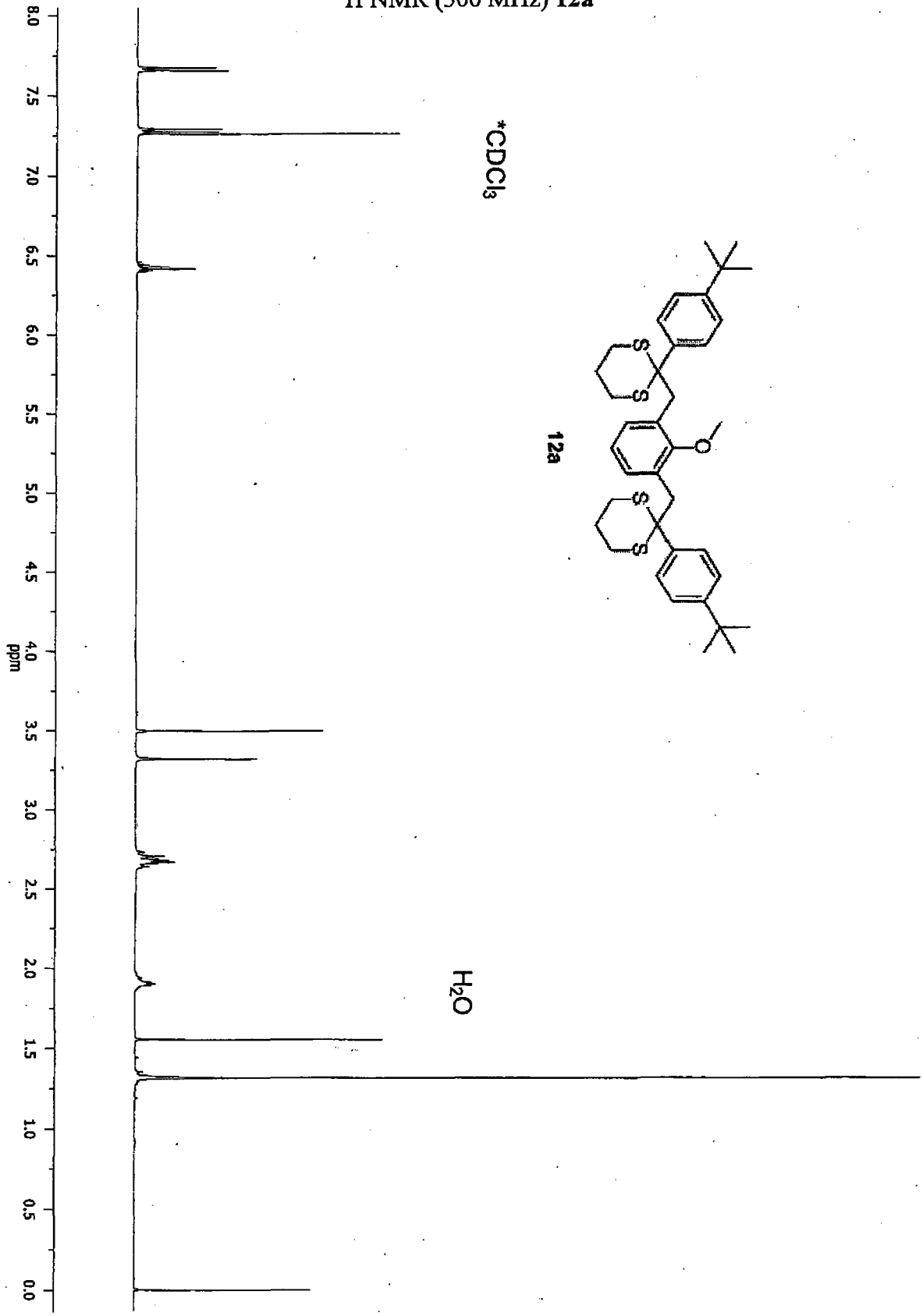

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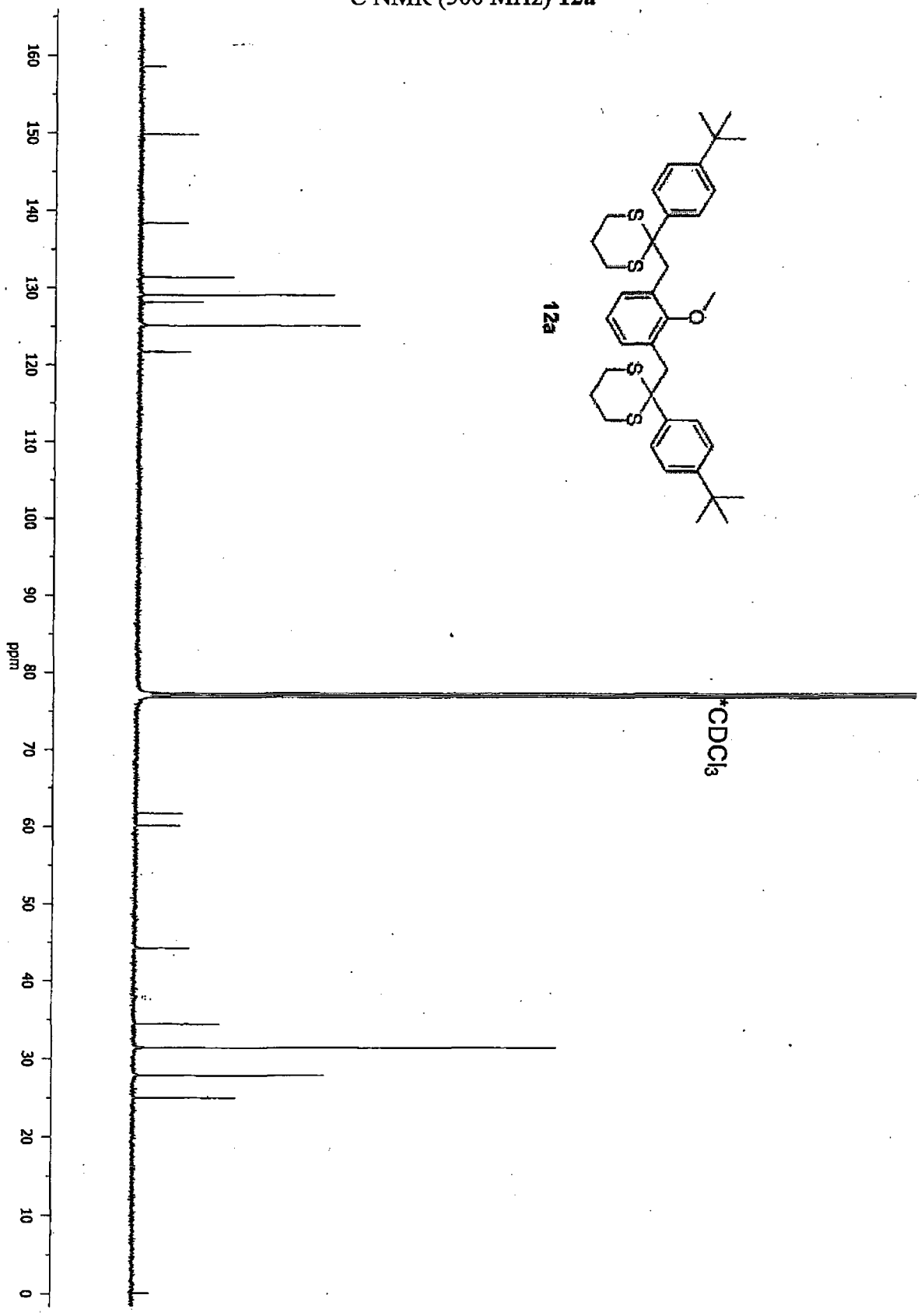
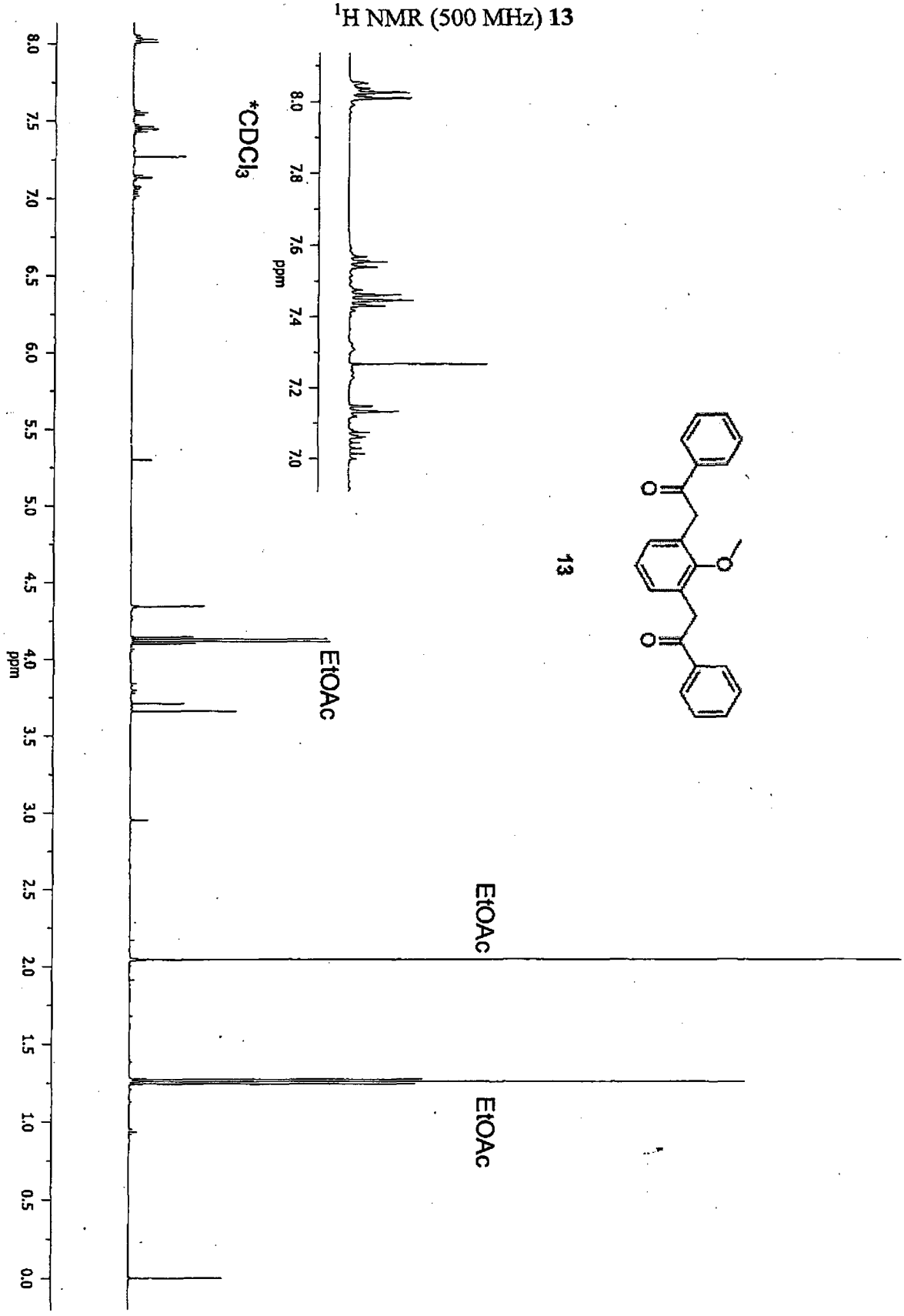
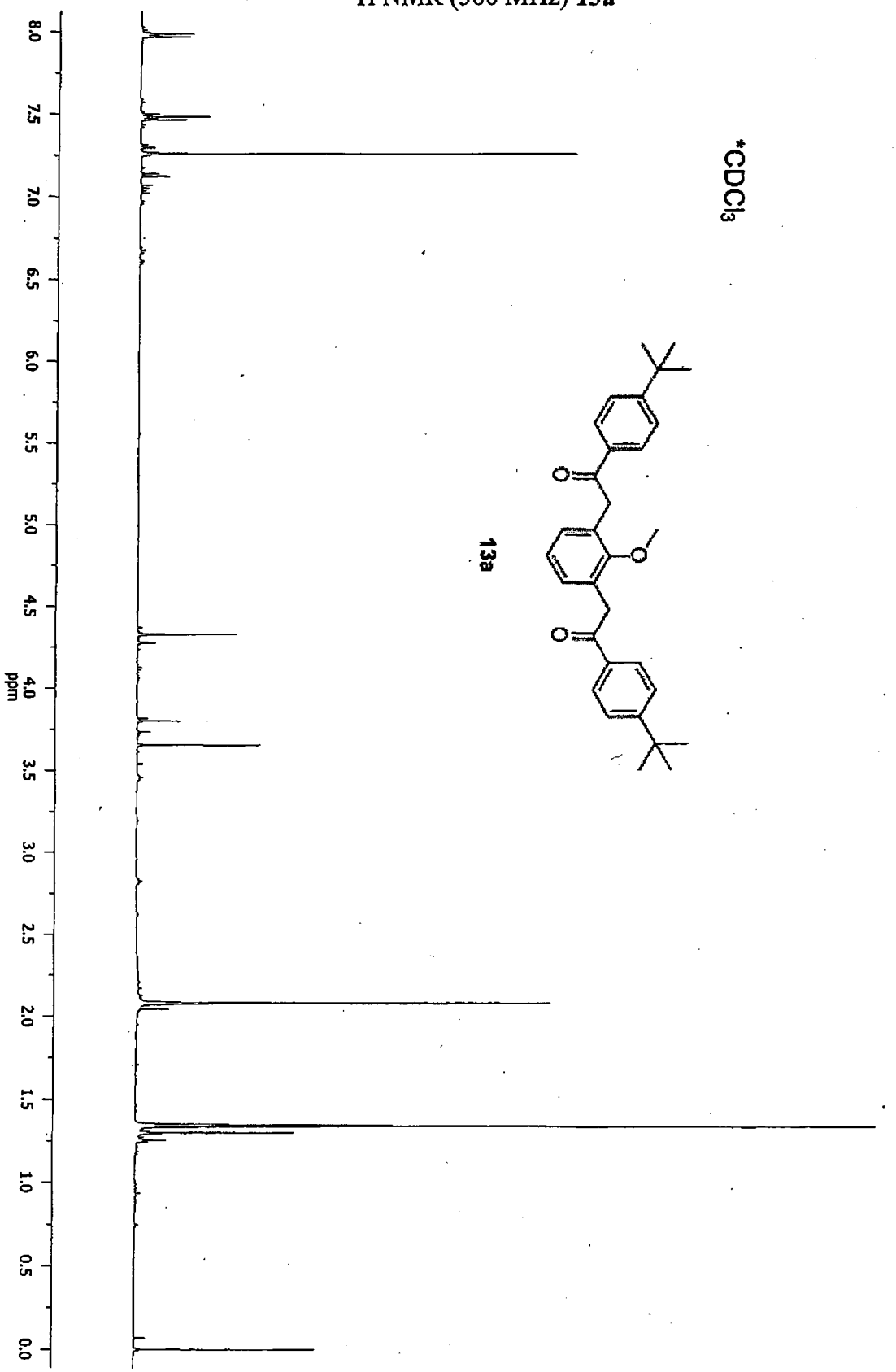


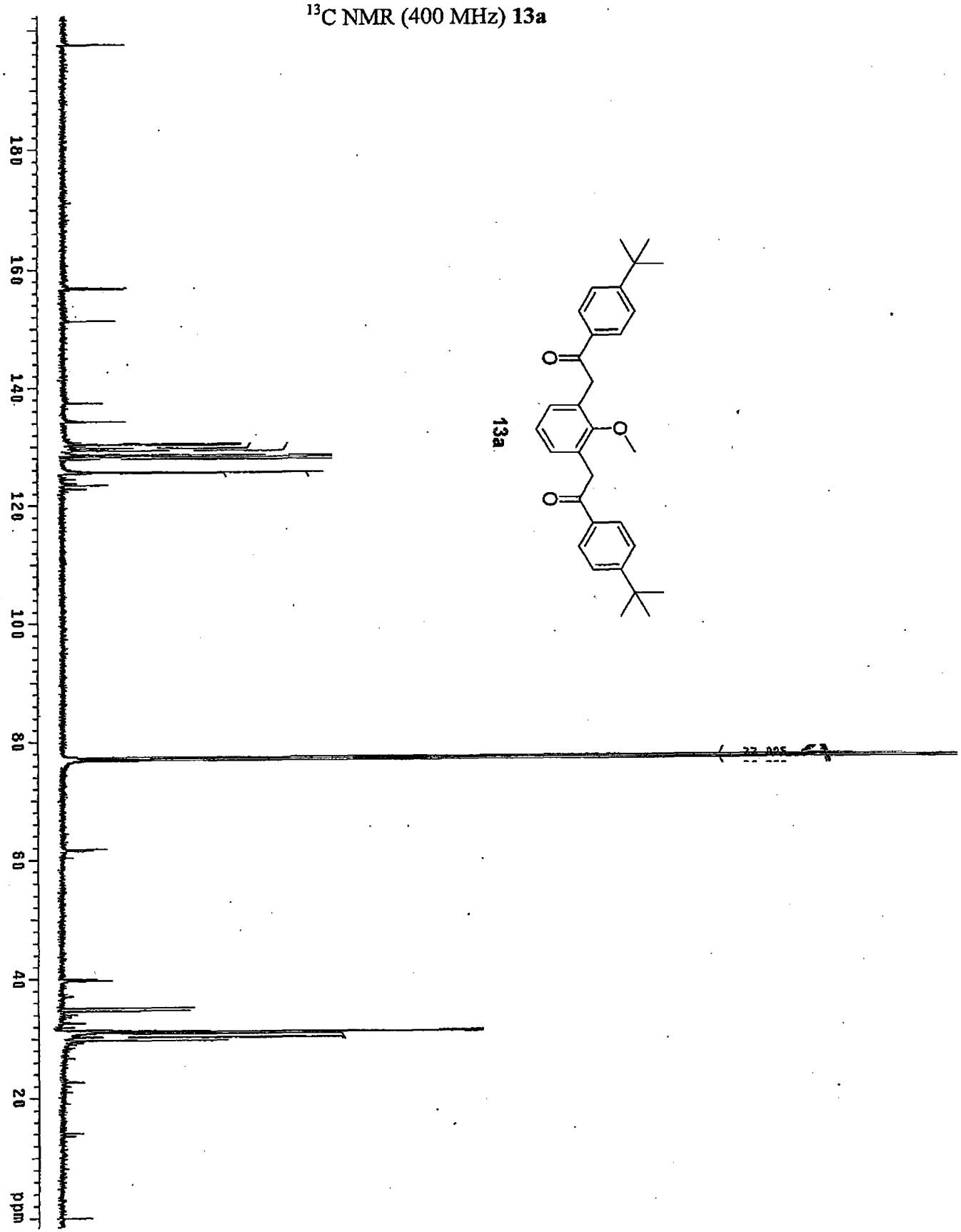
^{1}H NMR (500 MHz) **13**



^{1}H NMR (500 MHz) **13a**

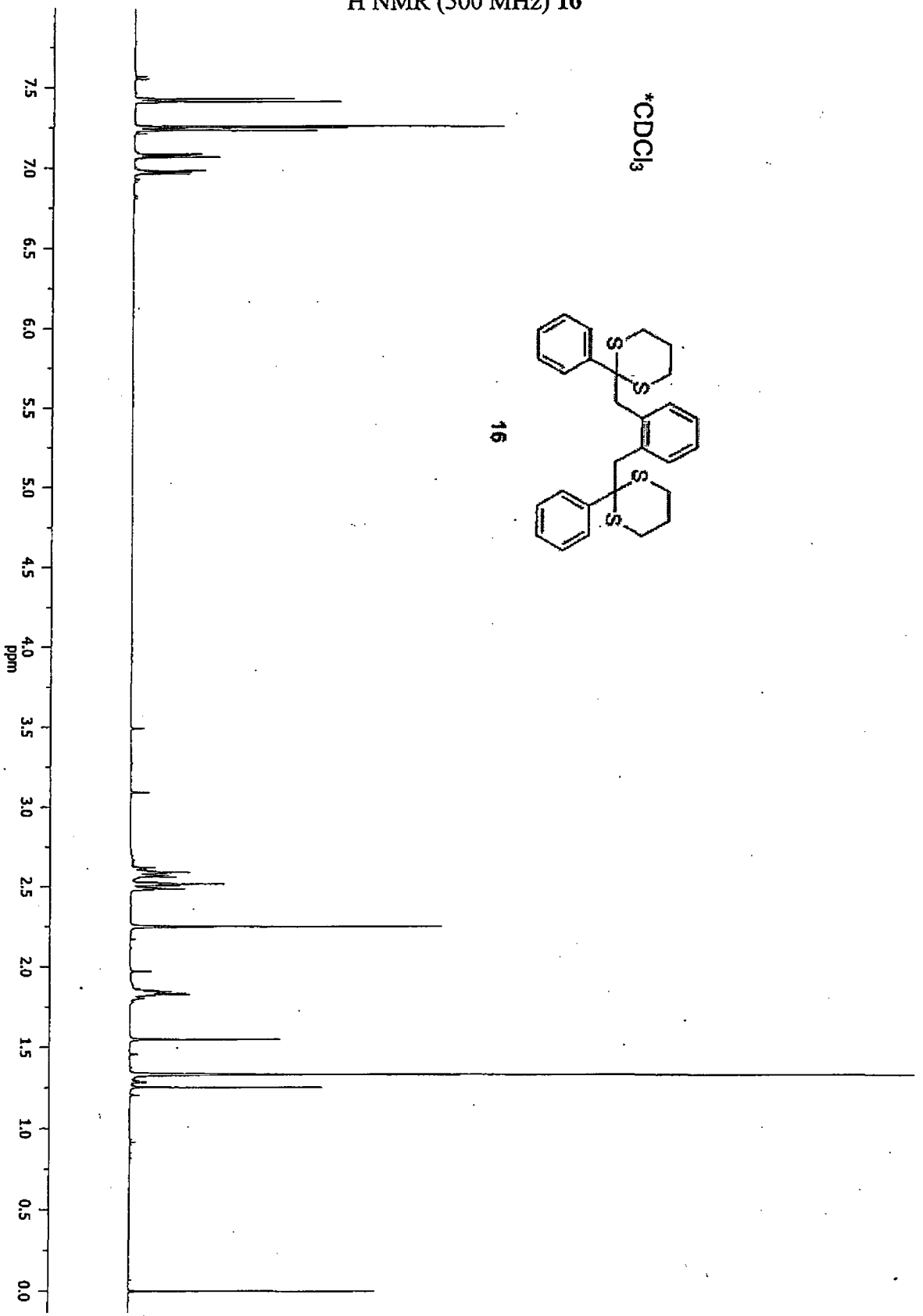


^{13}C NMR (400 MHz) **13a**

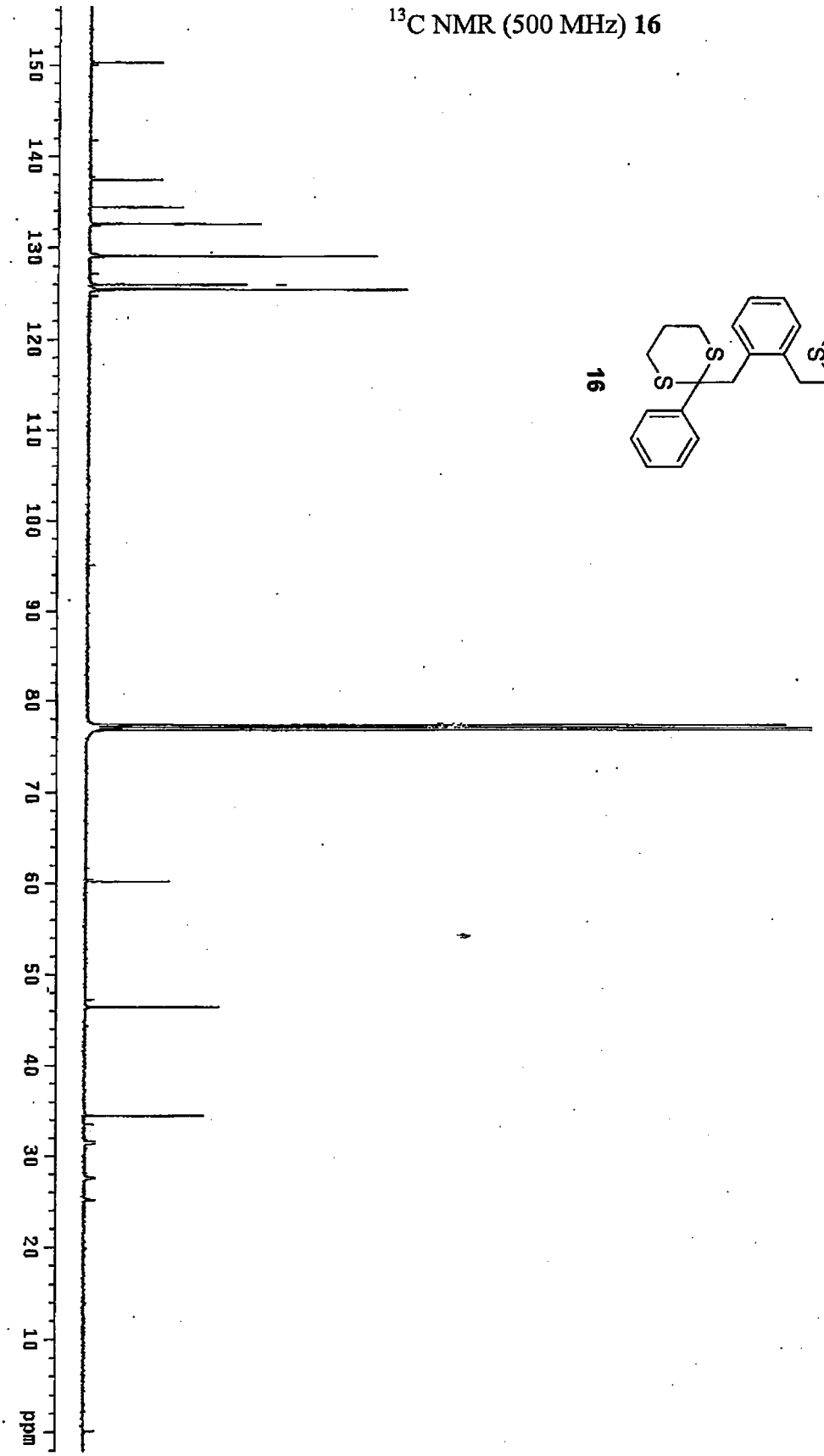


13a

^{1}H NMR (500 MHz) **16**

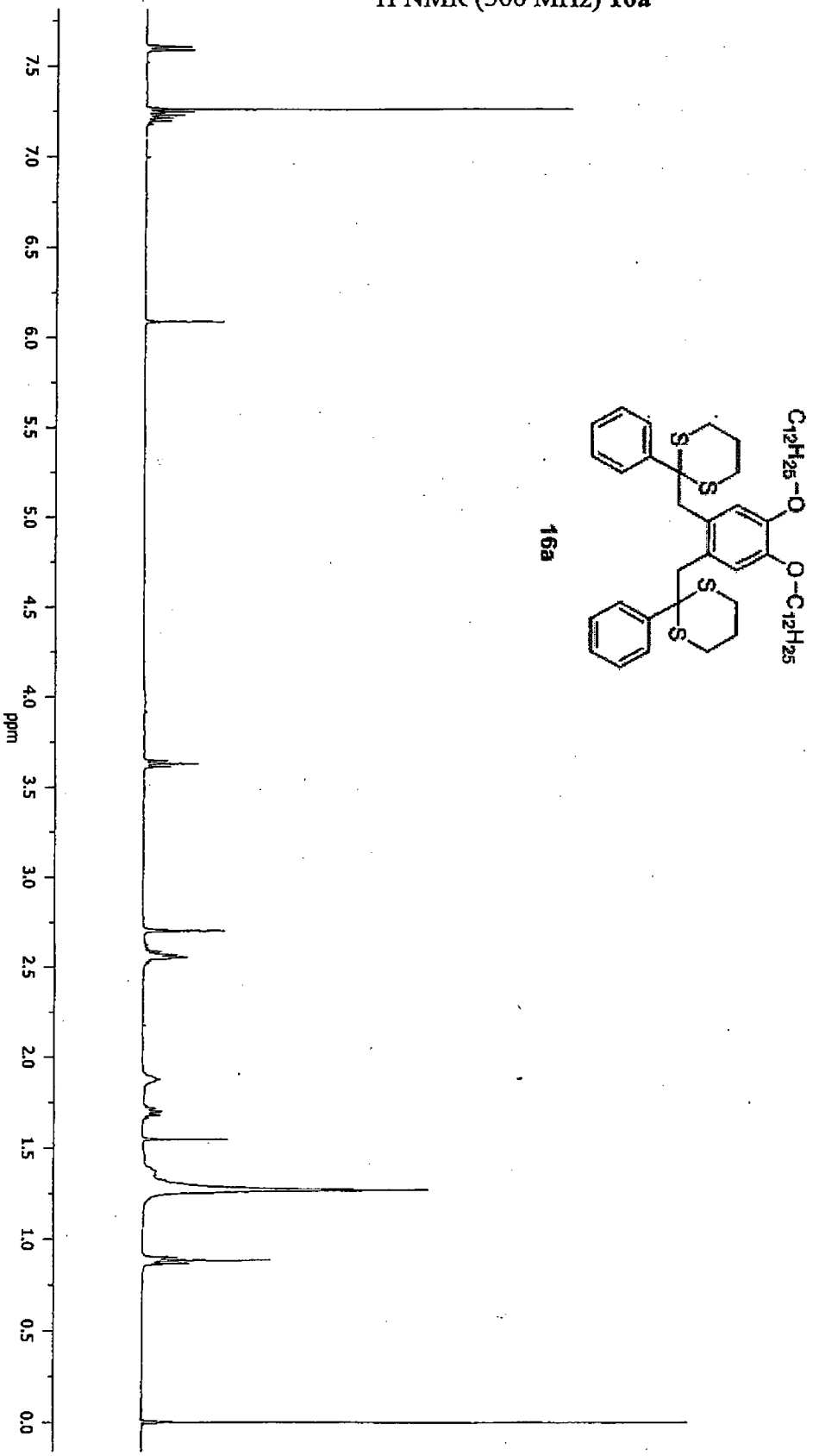


^{13}C NMR (500 MHz) **16**



16

^{1}H NMR (500 MHz) **16a**



16a